

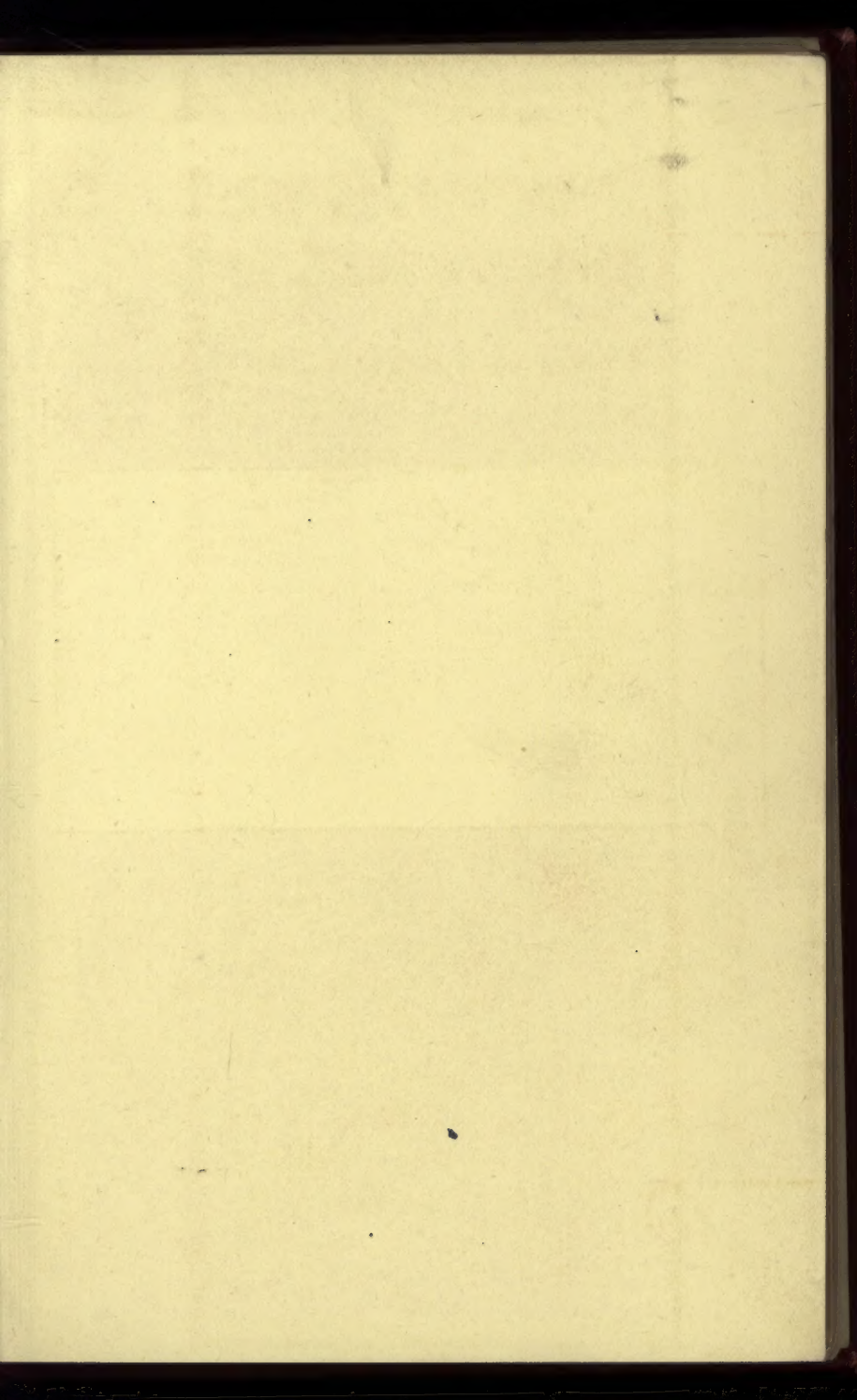
THE FIRST PRINCIPLES  
OF PHOTOGRAPHY  
BY  
CLEMENT J. LEAPER

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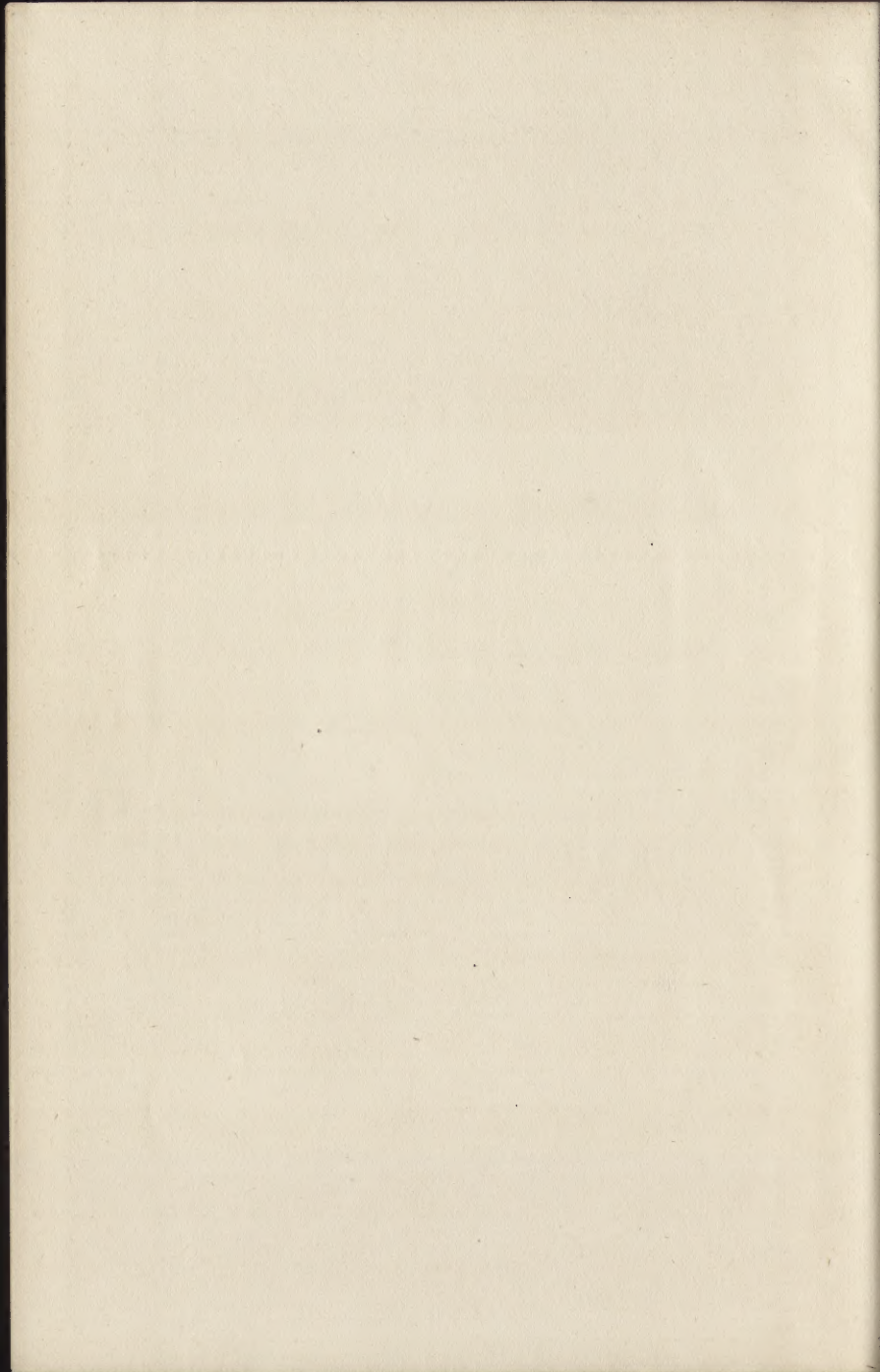
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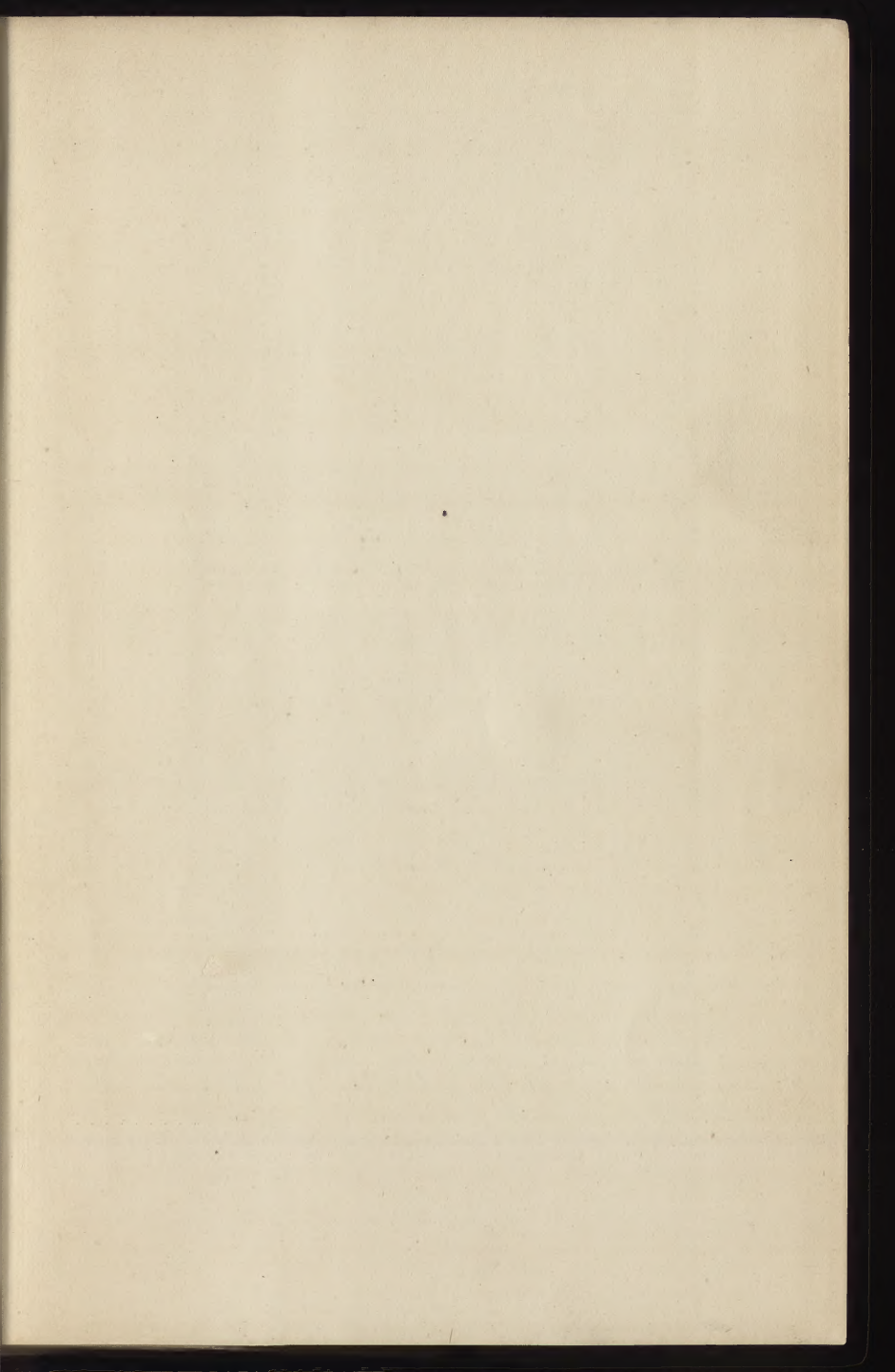
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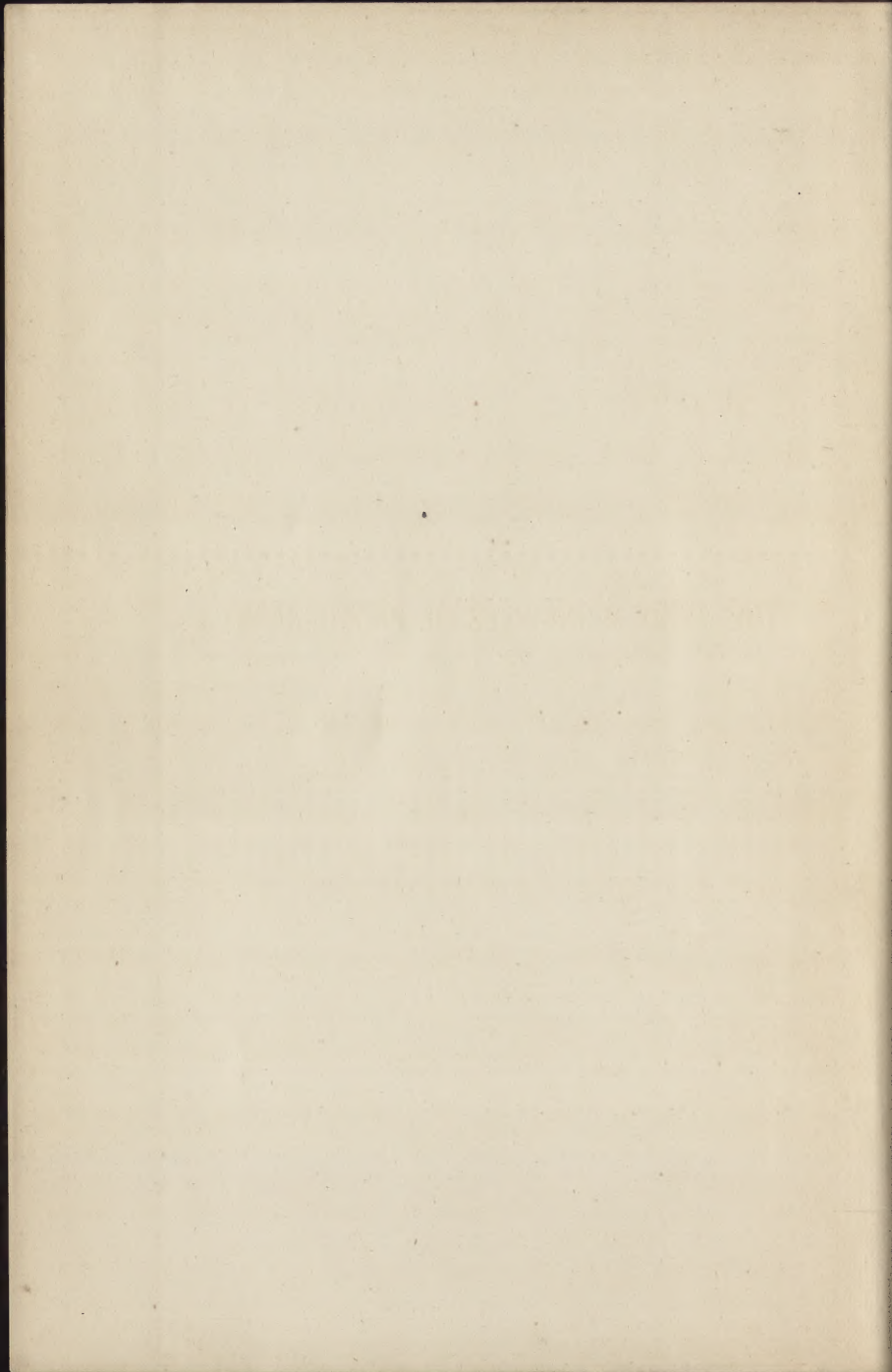








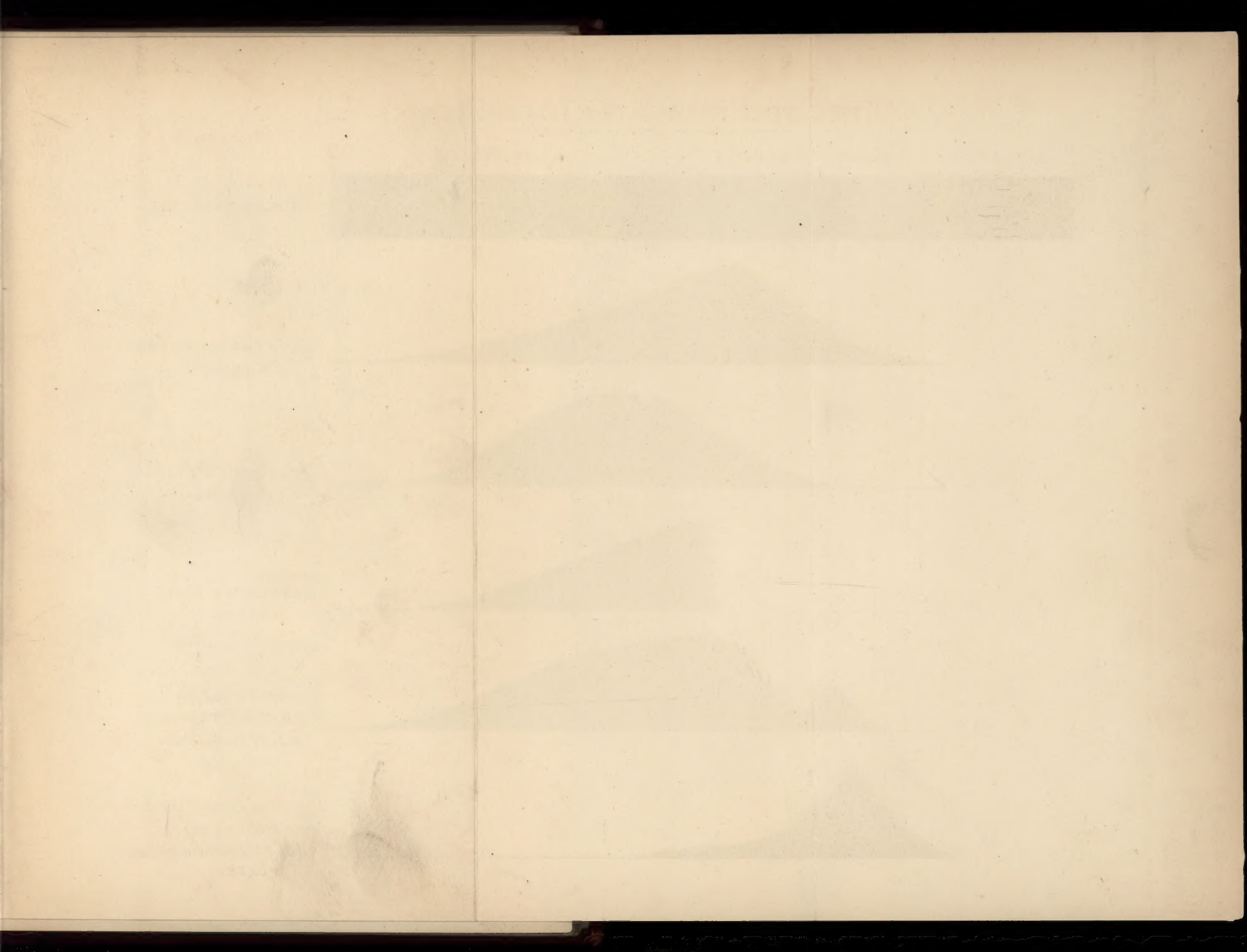




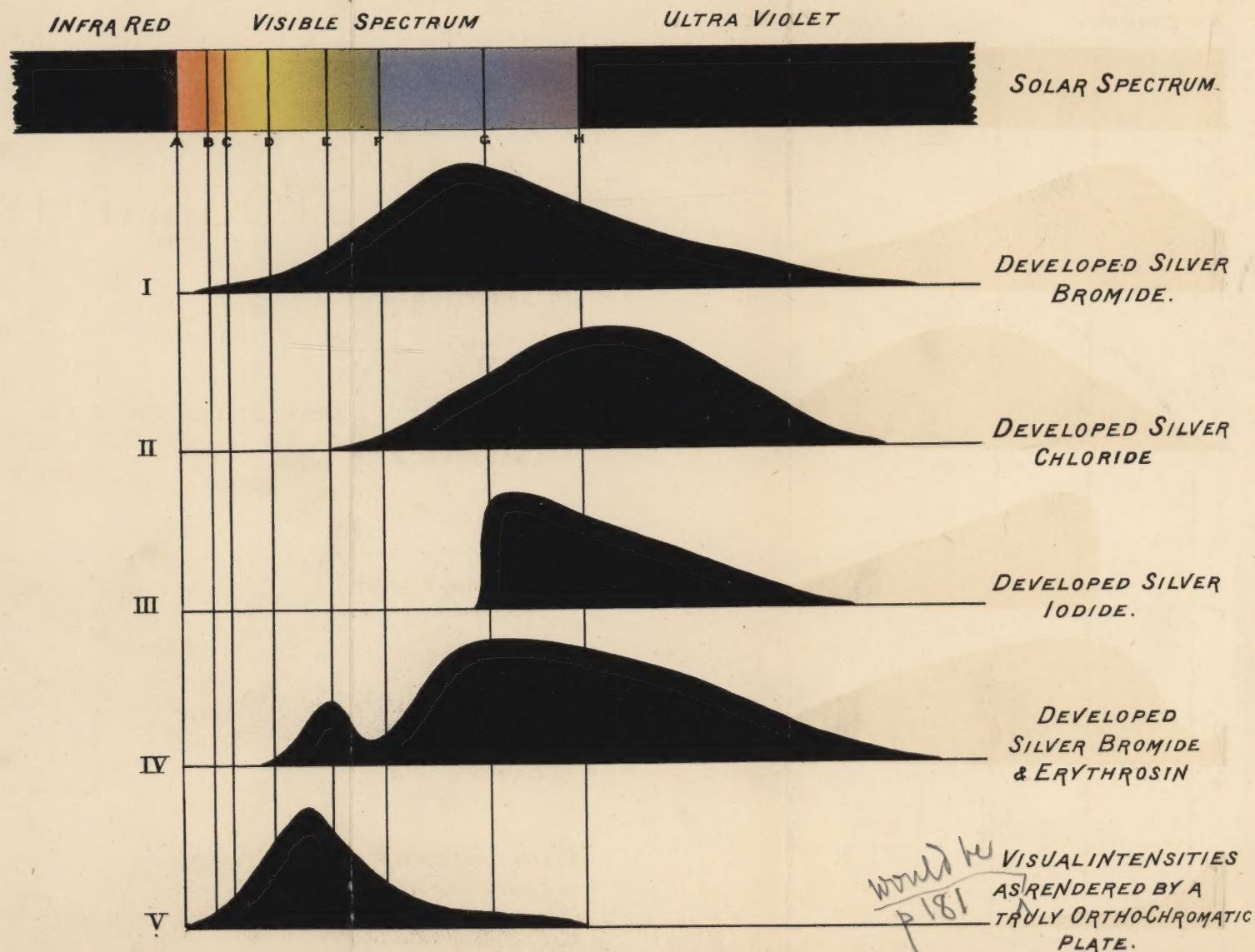
THE FIRST PRINCIPLES OF PHOTOGRAPHY.



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# THE SPECTRUM & ITS TEACHINGS





THE  
FIRST PRINCIPLES  
OF  
PHOTOGRAPHY:

AN ELEMENTARY TREATISE ON

THE SCIENTIFIC PRINCIPLES UPON WHICH  
PRACTICAL PHOTOGRAPHY DEPENDS.

BY

CLEMENT J. LEAPER, F.C.S.,

*Honoraryman, Medallist and Priseman in Photography City and Guilds of London Institute; late Instructor in Chemistry and Photography City of Dublin Technical Schools; Science Master at the Taunton and Bridgwater Technical Schools; Author of "Photography for Fun," "Experimental Photography," "Construction and Use of Photographic Lenses," "Materia Photographica," "Synoptical Tables of Inorganic and Organic Chemistry," etc., etc., etc.*

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## PREFACE.

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IN the following pages, I have embodied the substance of the course of lectures on photography annually delivered by me since 1882, first at the Dublin Mechanics' Institute and latterly at the City of Dublin Technical Schools.

In my treatment of the subject, I have in the main followed the admirable syllabus of the City and Guilds of London Institute, and to students preparing for the Institute's Examinations in Photography I believe this work will be of special service.

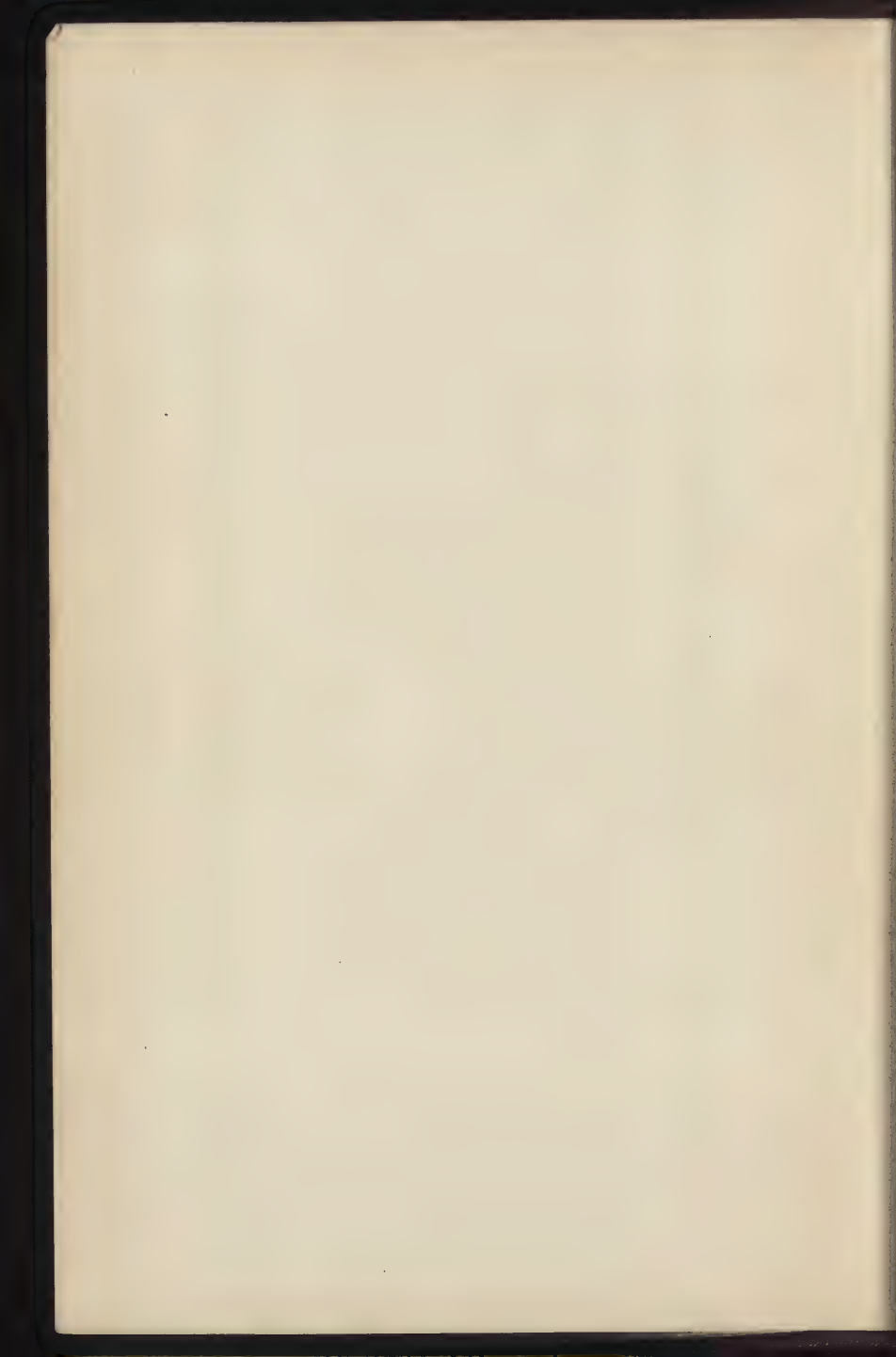
To help those who are without a teacher I have added a number of questions for self-examination, most of them taken from previous examination papers.

After careful consideration of the entire question I have adopted the somewhat revolutionary views of Messrs. Hürter and Driffield, but I must confess that much still remains to be done before a thoroughly satisfactory theory of the action of light upon sensitive substances is arrived at.

Evidence is not, however, wanting to show that we are nearing this desirable goal, and the close of the present century may possibly see this debated point placed on as firm a footing as the Laws of Newton in Mechanics, or as that of Avogadro in Chemistry.

19, Belvedere Road,  
Taunton.





# THE FIRST PRINCIPLES OF PHOTOGRAPHY

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## LECTURE I.

Dependence of Photography upon Optics and Chemistry—Light—The Hypothetical Ether—Transmission of Sound by Aerial and of Light by Ethereal Vibrations—Difference between Air and Ether—Wave Motion—Longitudinal and Transversal Waves—Unimportance of Precise Method of Originating Vibrations—Modes of Producing Artificial Light—Frequency as Limiting Sensations of Sound and of Light.

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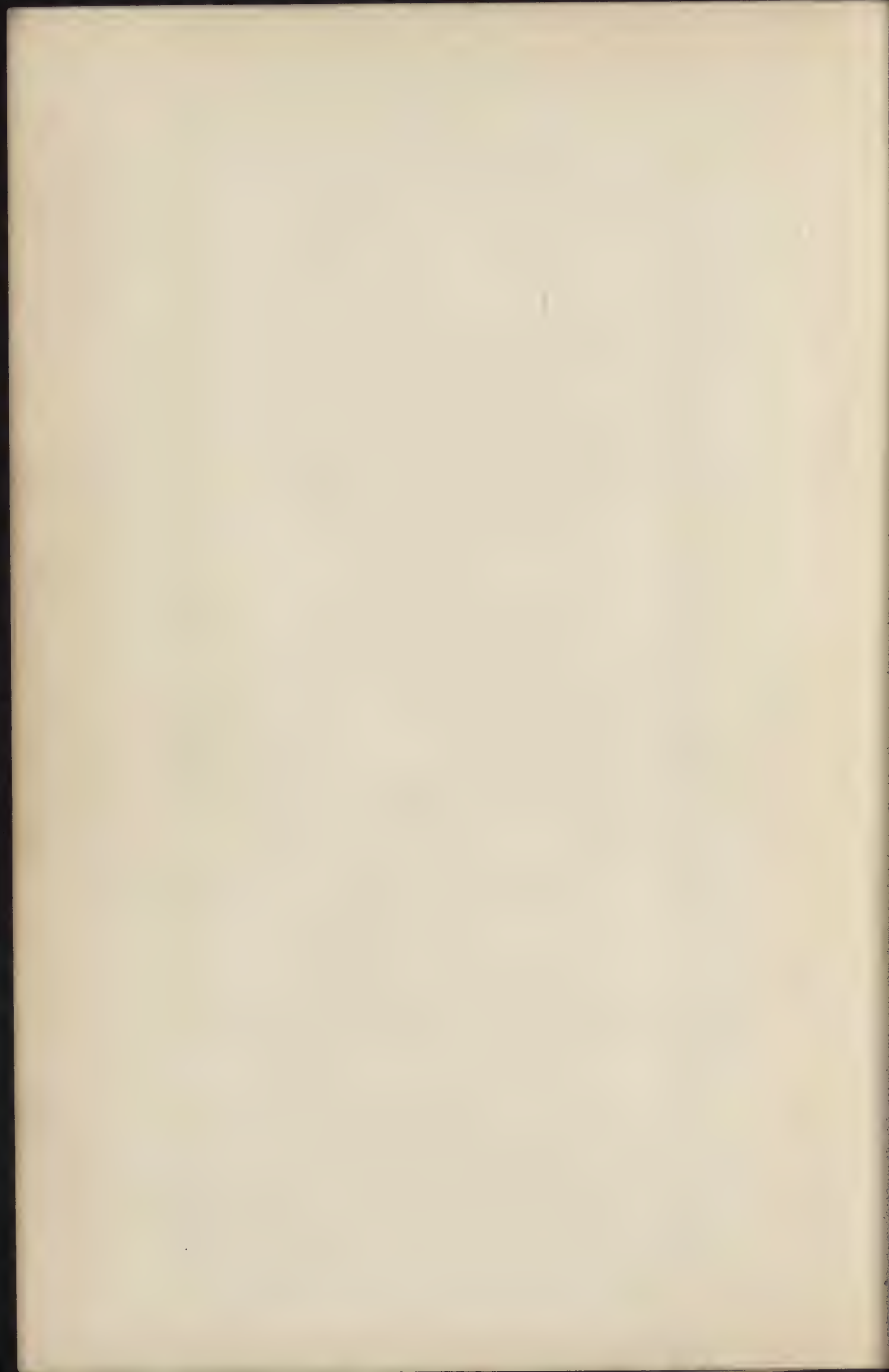
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# THE FIRST PRINCIPLES OF PHOTOGRAPHY

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## LECTURE I.

DEPENDENCE OF PHOTOGRAPHY UPON OPTICS AND CHEMISTRY—LIGHT—  
THE HYPOTHETICAL ETHER—TRANSMISSION OF SOUND BY AERIAL  
AND OF LIGHT BY ETHEREAL VIBRATIONS—DIFFERENCE BETWEEN  
AIR AND ETHER—WAVE MOTION—LONGITUDINAL AND TRANSVERSAL  
WAVES—UNIMPORTANCE OF PRECISE METHOD OF ORIGINATING  
VIBRATIONS—MODES OF PRODUCING ARTIFICIAL LIGHT—FREQUENCY  
AS LIMITING SENSATIONS OF SOUND AND OF LIGHT.

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**P**HOTOGRAPHY is the child of optics and of chemistry. Light enables us to lay the groundwork of our picture, and the judicious use of certain chemicals completes it. It follows, therefore, that to understand our subject we must learn something about the sciences upon which it depends, and, as light takes the initial step in the cycle of photographic operations, so optics has the first claim to our consideration.

Modern hypothesis tells us that light is the result of waves or undulations taking place in what we call the ether, and the reasoning adopted is well illustrated by the more easily observed phenomena of sound.

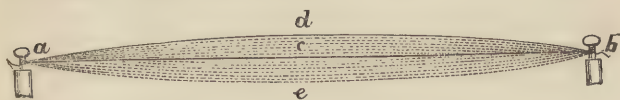


FIG. 1.—A VIBRATING STRING.

If this stretched string is pulled to one side (fig. 1) and then released, it vibrates to and fro. The musical note which it emits is plainly heard by all.

Here the vibrations of the string have been taken up by the surrounding air, and so transmitted to the ear, the drum of which is, in consequence, made to partake of the motion of the string. The most cursory examination reveals the fact that such a string actually vibrates, and more careful research proves that both the surrounding air and the recipient ear-drum vibrate with it.

Precisely as the drum of the ear will, when set in comparatively slow motion, convey to the brain the sensation of sound, so the retina of the eye, when made to vibrate with extreme rapidity, will convey to the brain the sensation of light. And just as the moving string originated aerial vibrations so will light, say that of this gas flame, set up ethereal ones.

In the case of the vibrating string the ponderable air is the medium or agent through which the impression is conveyed to the ear; in the case of the luminous flame hypothesis creates the almost imponderable ether, and then sets it vibrating to account for the cognate result.

Of the actual existence of air, and of the fact that it or some other ponderable medium is indispensable to the transmission of sound, we have ample evidence.

In this exhausted receiver I have a small bell capable of being set in motion by clockwork. On starting the mechanism no sound is heard, because no air is present in the portion of space surrounding the bell. But on gradually readmitting the air by opening the stopcock the sound, feeble at first, becomes louder and louder, and is heard with its full intensity when the receiver is full of air. So that, in the case in point, the presence of air is essential to the transmission of sound.

From this glass globe, hanging from one pan of our balance, the air has been exhausted, and the weights in the opposite pan exactly counterpoise the glass globe and brass fittings. But on opening the stopcock the pan containing the exhausted globe gradually descends, and to restore the equilibrium we must place weights in the opposite pan. Here the increase in weight is due to the air which has entered, and the experiment proves that the air through which sound is transmitted possesses weight.

In this exhausted globe I have, on the other hand, a fine filament of platinum wire, and on connecting the two copper wires on the outside of the globe, and in contact with the filament inside, with the poles of a battery, the platinum filament glows and emits light. Just as in the former case I readmit air by opening the stopcock, and you perceive that the brilliancy of the light does not increase in the slightest degree. Light, then, unlike sound, is transmitted through vacuous space; that is to say, the medium necessary for its transmission is, at least with the means of testing at our command, practically imponderable.

We have in the ether a something of whose existence we have no direct proof. We cannot see it, but we nevertheless believe that its existence is essential to vision, and although we cannot actually weigh it, indirect evidence points to the fact that this is due merely to the inadequacy of the means of weighing at our command.

It might, at first sight, appear that sound or light resulted from a motion of translation of air or ether particles from the vibrating source to the eye. Such is not, however, the case, the motion

taking the form, not of direct translation, but of a wave or undulation—a state of things well illustrated by the series of seven balls I have on the table, each capable of to and fro or of up and down motion independently of the rest. Let such a row of balls be situated at a certain distance from each other, and let each ball be capable of a to and fro motion quite independently of the rest.

Let A move to the right to such an extent as to decrease its distance from B to one-half its original amount. At the instant A reaches the limit of its excursion, let B move forward in a similar way towards C, A at the same time moving backward to its first position, and let C, D, E, etc., make corresponding to and fro excursions.

Under these circumstances, it is clear that, although each individual ball merely moves to and fro, a *wave* or undulation will appear to travel from A to G and back again.

Waves of this sort are said to be longitudinal, and the transmission of sound through air is effected by the to and fro motion of each particle of air existing between the sounding body and the ear.

But we have another and quite distinct form of wave motion.

Let the balls A, B, C, etc., be capable of up and down motion to the extent of, say, a quarter of an inch, and at the instant A has arrived at the limit of its downward excursion, let B begin to move downward whilst A is moving upward, the same state of things continuing to take place between B C, C D, and so on.

Then it is evident that under these new conditions a wave will also be propagated towards G and back again, the direction of which is now at right angles to the direction of motion of the particles themselves. Waves produced in this way are called transversal, and when transmitted through the ether from a luminous body to the retina of the eye result in the sensation of light.

To illustrate in another manner the difference between these two kinds of waves, I have a long rubber tube filled with sand, one end attached to the ceiling, and the other hanging free.

Along the tube, and at a distance of an inch from each other, are a series of small brass rings, which by their motion will render visible the motions of the different portions of the tube upon which they are strung. Taking hold in the right hand of the free end of the tube and stretching it somewhat with the left, I grasp the sixth ring from the bottom and pull down the tube from that point so as to stretch it to a greater extent above and to a lesser extent below. On now releasing the tube at the point held by the left hand you perceive the longitudinal wave travelling up the tube and reflected back from the top. The rings here evidently correspond to our row of balls moving to and fro.

Again grasping the bottom of the tube I give it a slight shake, and you now see the transversal wave travelling up and down, this state of things being the analogue of our row of balls moving up and down.

It may be taken as axiomatic that the precise manner in which the aerial or ethereal particles are set vibrating exerts within certain limits no influence on the final result, so far at least as the mere perception of sound or of light is concerned.

In the case of the stretched string, its elasticity caused it, when pulled to one side, to revert to its original position, beyond which it was then carried by the momentum of its own moving mass, its elasticity again causing it to move back to nearly its starting point, and this to and fro motion resulted, provided the string was neither too thick nor too thin, too long nor too short, in the sensation of sound. But we can produce the same sensation in quite a different way. Around the periphery of this stout cardboard wheel, mounted on an axis so as to admit of being spun round, a number of small holes are pierced, and nearly touching the revolving circle of holes is a fine glass tube. Although the wheel is in motion, no sound is heard, but on blowing through the glass tube we obtain a musical note, each puff of air passing through the hole opposite the glass tube corresponding in this case to the forward or backward motion of the vibrating string.

Similar results hold good in the case of light. We may set the ether vibrating by causing an intensely hot but almost colourless flame to impinge upon an incombustible solid, as in the case of the so-called limelight. Or, as in the case of burning magnesium, we may cause the intensely hot flame to produce its own incombustible solid, viz., the magnesia resulting from the burning of the magnesium itself.

In an ordinary gas flame, considered as a source of light, the solid is the soot or carbon, which, because combustible only when in contact with air, cannot burn away inside the flame. By admitting air to the interior of such a flame, as is done in the Bunsen burner, we cause it to become practically non-luminous, just as a burning jet of oxygen and coal gas would, without the glowing cylinder of lime, be practically useless so far as light is concerned.

In the arc electric light we have another means of originating ethereal vibrations, the result being in this case mainly due to the volatilisation of a portion of the carbon, this vapour being then caused to glow by the passage of the electric current through it. Since carbon is a combustible substance, the pencils forming the arc gradually burn away, but if, instead of vaporious carbon, we place a fine filament of solid carbon in a vacuum and pass the current through it we get an analogous result, and the arrangement now constitutes an incandescent electric lamp.

In alluding to the vibrating string I made, as you will remember, the reservation that it must be neither too long nor too short, too thin nor too thick. Examined a little more closely this means that to convey to the ear the sensation of sound the string must move at a rate which is neither too small nor too great. An experiment with the revolving wheel illustrates this. Causing a



current of air to impinge upon the row of holes I make the wheel revolve with extreme slowness, and although there is no doubt but that aerial waves have been set up the ear receives no sensation of sound. Increasing the speed a point is soon reached at which a low hum is apparent, and this is changed to a higher and higher musical note as the wheel is spun round with gradually increasing velocity.

Now, since the only factor which changes during the experiment is the velocity of rotation, and as this influences the number of puffs of air in a given interval of time, it follows that if aerial vibrations are to be appreciated as sound, they must succeed each other with sufficient rapidity. We put this matter in other words by saying that vibrations of less than a certain minimum frequency are inaudible.

If we had a means of causing the wheel to rotate at an enormous speed, we should again find that if the interval between two puffs of air was such as to produce vibrations of more than a certain maximum frequency no sound would be heard.

The latter part of the experiment is readily performed in another way. Here I have a whistle, the pitch of the note yielded by which can be varied by altering the distance between the *embouchure* and a movable piston sliding within the tube. On sounding it so as to produce an audible note you will notice that the sensitive flame on the table quivers, the quivering of the flame being an optical test of the fact that aerial vibrations are being produced.

On moving the piston nearer to the *embouchure* a point is soon reached at which the whistle yields no audible sound when blown into, but the motion of the sensitive flame reveals the fact that, although the ear hears no sound, aerial disturbance is still going on.

We may, then, have aerial vibrations of any frequency we please, but, unless the actual frequency falls within a certain maximum and minimum, such vibrations are not appreciated as sound.

A result analogous to this takes place in the case of ethereal vibrations.

Sending a feeble current of electricity through this long platinum wire, the eye perceives no change in it, although the finger applied to the wire reveals the fact that it is perceptibly warmer than before. Increasing the current, we reach a point at which the wire is too hot to hold, hot enough, in fact, to char paper, although as yet it emits no light. Gradually increasing the current, we soon reach a point at which the wire becomes first red-hot, then white-hot, and finally melts.

Here the ethereal vibrations set up by the gradually-heated platinum were of too small frequency at first to affect the eye, but by increasing that frequency we soon reached the minimum limit.

The platinum wire is just like matter in any of its forms made

up of molecules which vibrate at a rate dependent partly upon their nature and partly upon the temperature of the mass of which they form part. These vibrating molecules, although very minute, will, when vibrating, cause the surrounding ether to vibrate with them just as the grosser vibrating string caused the air to vibrate.

If the rate of vibration is below a certain minimum, no light is perceived, because the eye, like the ear, is unaffected by vibrations of less than a certain frequency, but if the rate of vibration is made in any way to exceed the limit, then the eye is, like the ear, made cognisant of the fact.

#### SUMMARY OF LECTURE 1.

A sounding body is *heard*, owing to its *motion* communicated to the *air* being taken up by the drum of the *ear*.

A *luminous* body is *seen* owing to its *motion* communicated to the *ether* being taken up by the retina of the *eye*.

Sound and light are both the result of motion.

*Air* is *ponderable*, and can be proved in a direct and indisputable manner to *exist*.

*Ether* is *practically imponderable*, and can be proved to *exist* in an *indirect* manner only.

The *existence of air* is a *fact*, the *existence of ether* is an *hypothesis* assumed to *explain facts*.

*Sound* is not transmitted through a *vacuum* owing to the absence of the essential ponderable medium.

*Light* is transmitted through a *vacuum* because the ether is assumed to be as truly present in a vacuum as in a plenum.

The *motion* causing sound or light is not a *motion of translation*.

A particle translated from one point A to another B travels over the *entire space* from A to B.

A *series of particles*, causing by their motion a *wave* to travel from A to B, individually *move* if the wave is longitudinal over only a mere *fraction* of the space of A to B, and if the wave is transversal do not move in the direction A B at all, but at right angles to it.

Each *particle* in a row of moving particles constituting a wave *moves independently* of the rest.

In *longitudinal* waves the *direction of the wave* coincides with the *direction of the particles* when at rest.

In *transversal* waves the *direction of the wave* is at *right angles* to the *direction of the particles* when at rest.

A longitudinal wave is produced along a rubber tube by stretching one portion of the tube in the direction of its length, and then releasing that portion, a transversal wave by stretching one portion of the tube in a direction at right angles to its length and then releasing it.

*Aerial vibrations* of a *certain frequency*, no matter how produced, result in *sound*. A stretched string moving to and fro at a certain

rate, or a series of puffs of air succeeding each other at the same rate, produce the same effect upon the ear.

*Ethereal vibrations* of a *certain frequency*, no matter how produced, result in *light*. A hot flame impinging on a cylinder of lime (limelight), a hot flame producing its own incombustible solid (magnesium light, or a luminous jet of coal gas), a vapour caused to glow by electricity (arc light), or a solid caused to glow by electricity (incandescent light), produce, practically, the same effect upon the eye.

Aerial vibrations to result in sound must be neither too rapid nor too slow. *Ethereal vibrations* to produce *light* must also fall *within certain limits*.

## LECTURE II.

SYNTHESIS AND ANALYSIS OF A MUSICAL CHORD—PRISMATIC ANALYSIS OF WHITE LIGHT—THE SPECTRUM—DIFFERENCE BETWEEN SPECTRUM YIELDED BY INCANDESCENT SOLID AT DULL REDNESS AND SAME SOLID AT VIVID WHITENESS—RED END OF SPECTRUM THE RESULT OF ETHEREAL VIBRATIONS OF SMALLER FREQUENCY THAN VIOLET END—CONNECTION BETWEEN VELOCITY OF PROPAGATION, LENGTH, AND FREQUENCY OF A WAVE—SMALL FREQUENCY SYNONYMOUS WITH LONG WAVE, GREAT FREQUENCY WITH SHORT WAVE—SIMILAR AND OPPOSITE PHASES OF PARTICLES IN A WAVE—INTERFERENCE OF PARTICLES ANY UNEVEN NUMBER OF SEMI-UNDULATIONS FROM EACH OTHER—SILENCE THE RESULT OF INTERFERENCE OF AERIAL, DARKNESS THE RESULT OF INTERFERENCE OF ETHEREAL PARTICLES—PRIMARY AND SECONDARY WAVES—MEASUREMENT OF WAVE LENGTH OF RED LIGHT.

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IT has been already pointed out to you that for the ear to hear or for the eye to see, the aerial or ethereal vibrations causing what is heard or seen must fall within certain limits

We have now to learn what effect variations within these assigned limits will have upon any particular result.

Causing once more my syren to slowly rotate whilst a current of air is being directed against the holes in its periphery, you hear a low musical note, and on increasing the speed of rotation this note gradually rises in pitch, the rise in pitch evidently corresponding to increased frequency.

Maintaining the speed fairly constant means fixity of pitch, and we express this result by saying that a musical note of a definite pitch corresponds to a fairly definite rate of vibration.

Bowing these four tuning-forks in succession you hear the notes do—mi—sol—do, and the aggregate of the four notes gives what musicians call a chord, and in which a practised ear could detect each component note. By bowing only one fork at a time I could bring my syren into unison with that note by suitably altering the velocity with which it revolves, and so obtain its frequency.

We call, then, a simple note one of definite frequency, and a chord the result obtained when a series of simple notes are sounded together, or we might put the latter statement in other words by saying that a chord is the result of aerial vibrations of various frequencies acting simultaneously upon the ear.

Now white light is, like a musical chord, the result of ethereal vibrations of various frequencies acting simultaneously upon the

eye, but this organ, unlike its kindred ear, requires extraneous aid to enable it to resolve the chord of light into its component parts. Such aid is afforded by a prism, and I can prove the complex nature of white light in the following manner:—

In front of the condenser of my lantern is a narrow slit, which, illuminated from behind by the incandescent lime, is projected upon the screen by the front lens of the lantern as a narrow band of white light.

Placing in the track of the beam a hollow glass prism filled with colourless carbon disulphide you perceive that the white band is broadened out into the brilliantly-coloured parallelogram projected upon the other screen, placed considerably to one side of the first (see frontispiece). You will notice that in this spectrum, as the coloured parallelogram is called, we have in the main seven colours, each colour occupying a considerable space in the spectral band. What is the precise meaning of the relatively large space which each colour occupies?

Reverting again to our syren, I cause it to rotate at such a speed as to bring the note it yields into what the unaided ear would call unison with this particular vibrating fork. Having done this, I render the motion first somewhat slower and then somewhat faster, and although by so doing the frequency of the note yielded by the syren must have been increased or decreased, yet the ear fails to detect any want of agreement. In other words, the unaided ear appreciates as the same musical note a series of notes whose maximum and minimum frequencies are comprised within certain limits.

So it is precisely with our spectral colours. The breadth of any individual band of colour represents the extent to which the ethereal frequencies giving rise to that colour may vary without ceasing to exert an identical impression upon the unaided eye.

Beginning at the furthest visible end of the comparatively broad violet band, we say that ethereal vibrations of frequencies comprised within limits measured by the distance between this and the extremity of the indigo produce that sensation which we call a violet colour, but if that frequency is altered to a sufficient extent the eye receives in succession a series of impressions corresponding to indigo, blue, green, yellow, orange, and red, each of these colours affecting the retina in a special way, independently within certain limits of variations in the frequencies of the ethereal vibrations giving rise to each colour.

In the case of musical notes we know that low pitch means small and high pitch great frequency, and since we have compared our spectrum to a musical chord, the sensation produced upon the eye by the violet end of it must be the result of ethereal vibrations whose frequencies are greater or lesser than those of the red at the opposite end.

How are we to determine which end corresponds to the lesser and which to the greater frequency? Since we cannot, as with



the notes in a musical chord, match each colour with another, the frequency giving rise to which is known to us, we must attack this problem in a different way.

Substituting in my lantern a fine platinum wire for the incandescent lime, I pass a feeble current of electricity through the wire so as to cause it to glow at a dull, red heat. Careful examination of the screen upon which the spectrum previously fell now reveals the fact that the red band only is apparent, and that not very distinctly. Gradually increasing my battery current, so as to cause the wire to glow more and more brightly, you notice that the orange appears; the red not, however, disappearing, but showing up more brightly; whilst, by still further increasing the current, I cause the yellow, green, blue, indigo, and violet to appear in succession, and when the entire spectrum is visible, opening the lantern door reveals the fact that the wire is now at a white heat.

We conclude from this that just as by gradually increasing the velocity with which the disc of our syren first revolves the notes of lowest frequency are first heard, so that part of the spectrum which is first seen when the temperature of a solid is gradually raised, viz., the red, is that portion corresponding to the least rapid vibrations of the ether.

The evidence upon which we base this conclusion is, it is true, indirect, but will be subsequently corroborated by the actual measurement of the ethereal frequency giving rise to any particular ray.

You will remark that the red rays or those of small frequency make a smaller angle with the original direction of the light than do the violet rays corresponding to a greater frequency. We put this into scientific language by saying that the least refrangible rays have smaller frequencies than the more refrangible ones.

We must now learn how the precise length of each wave is measured, and here again our acoustical analogies come to our aid.

Let us assume that this particular fork makes, when vibrating, a complete to and fro excursion in one second of time. Then, under these circumstances, the aerial wave it produces will also take one second to travel a certain distance forward and back again. It is true that the precise distance travelled over by the aerial wave will be much greater than that travelled over by the prongs of the tuning-fork giving rise to it, but the time for a complete to and fro vibration is necessarily the same in both cases, since the aerial column vibrates synchronously with the prongs of the fork.

Now the velocity of sound in air is capable of direct measurement, and has been found experimentally to be at the temperature of this room 1,120 feet per second.

Since the prongs of the tuning-fork took one second to travel to and fro, the wave propagated through the air will also take one second to reach the limit of its excursion and back again, i.e., the wave will travel forward for half-a-second, and backward for the

next half-a-second. But since sound travels 1,120 feet in one second, it is clear that this must be the length of the wave, which is, you will remember, the distance travelled over in both directions, *i.e.*, forwards and backwards, or *vice versa*.

If, instead of making a complete vibration in one second, the fork had completed its vibration in half a second, then clearly the length of the wave in air would have been  $\frac{1120}{2}$ ; or designating by  $N$  the number of vibrations made in one second by the prongs of any particular fork, then  $\frac{1120}{N}$  gives the length of the aerial wave these vibrations would generate.

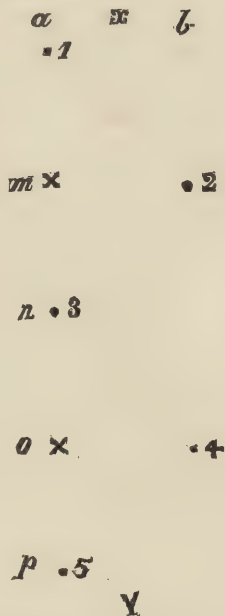


FIG. 2.—POSITION OF PARTICLES IN A WAVE.

Designating the length of the wave by  $L$ , we may then express the general result by the equation  $L = \frac{V}{F}$  in which  $L$  is the length of the wave in any medium expressed in feet,  $V$  the velocity of sound in the same medium also expressed in feet, and  $F$  the frequency of the vibration giving rise to the wave.

It is easy to see from this, that the medium remaining the same, a high frequency corresponds to a short wave and a low frequency to a long one.

To pass from aerial to ethereal particles, let the dots 1 5 in fig. 2 represent the position at any instant of time of a row of ether particles vibrating with identical frequencies through the space between  $a$   $b$ .

Then, since each particle moves through a space equal to  $a$   $b$  and back again,  $a$   $b$  equals the length of a semi-vibration, and  $2 a b = W L$ , or that of a complete to and fro vibration.

Now, an inspection of the figure will easily reveal the fact that at any instant of time *all* the particles are not moving in the *same direction*.

Let us take, for instance, the period of time just after that represented. Then 1 3, 1 5 will be both beginning to move to the right, but 1 2, 1 4 will be moving, one to the right, the other to the left. We express this result by saying that particles 1 3, 1 5 are in similar, and 1 2, 1 4 in opposite phases.

Assuming, as has been done in the figure, that the distance from particle to particle when in the same line, viz.,  $a$   $m$ , equals that of a semi-vibration, viz.,  $a$   $b$ , we see that particles 1 2, 1 4, distant from each other 1 or 3 semi-vibrations, are in opposite phases, and a moment's consideration would reveal the fact that the same would hold good with particles distant 5 7 9, or any *uneven* number of semi-vibrations from each other.

Again, we have learnt that the particles 1 3, 1 5 distant from each other 2 or 4 semi-vibrations are in similar phases, and the same result would of course obtain with particles 6, 8, 10, or any *even* number of semi-vibrations from each other.

Let us assume that a luminous point of monochromatic light, *i.e.*, of light the result of vibrations of definite frequency, is situated at  $x$  in fig. 2, and that the eye placed at  $y$  receives a ray of light emitted from that point.

Then the figure represents what occurs with a single row of particles, and it is clear that, although 1 2, 1 4 are in opposite phases, they do not impede each other's motion.

But if, instead of a single row of ether particles limited in number and vibrating in planes parallel to each other, we had actually to deal with a practically unlimited number of ether particles vibrating in all planes, then it is clear that contiguous particles in opposite phases and vibrating in the *same* plane would impede each other's motion, provided the distance from one particle to another in the same plane equalled one, three, five, or any uneven multiple of the semi-vibrations giving rise to the light at  $x$ .

Just as sound is the outcome of the motion within certain limits of aerial particles, and silence results when this motion is impeded, so ethereal particles which, when vibrating, give rise to light will, when their motion is stopped, convey only the impression of darkness.

What reason have we for assuming that aerial or ethereal particles vibrate in all planes?

Representing the *direction* of a wave of sound or light by a straight line, it is easy to see that if the wave motion resulting in either of the sensations were propagated merely in radial lines from the centre of disturbance, the ear or eye placed at a certain

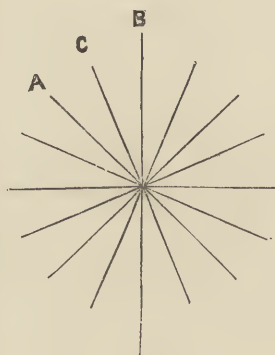


FIG. 3.—WAVES DIVERGING FROM A COMMON CENTRE.

distance, say between A and C (fig. 3), beyond that centre would fail to receive any impression, whilst by altering its position to A or B the impression would again be received. Now nothing of the sort occurs in practice, and it follows, therefore, that the preceding diagram is not an exact representation of the actual state of affairs.

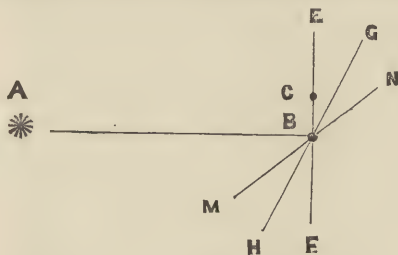


FIG. 4.—PRODUCTION OF SECONDARY WAVES.

In fig. 4 let A be the luminous point from which a wave emanates in the direction A B, and let B represent a particle of the ether which at one instant of time is at B and at the next at C,



from which position it once more returns to C. Then it is clear that, in addition to the primary wave moving forward in the direction A B and due at B to the up and down motion of the particle B, we shall have also a series of secondary waves in the directions G H, M N, having their origin at B, and due to the fact that the up and down motion of B will cause the contiguous particles along M N, B G, to partake of that motion.

What is true of a single ether particle must be true of all other particles, hence we learn that every ether particle is the centre of another series of waves propagated in all directions from the first particle as a centre.

Arranged in the path of the spectrum projected by the lantern I have two narrow slits at a considerable distance from each other, the width between the jaws of each slit being capable of alteration at will. Causing the red end of the spectrum to fall upon the first slit, I look at it through the second and see at the centre a vivid rectangle of red light, and right and left of this another series of rectangles, gradually decreasing in brightness, and separated from each other by intervals of darkness. Moving the slits so that I see the violet end of the spectrum, I find that the violet rectangles are narrower and closer together than the red ones.

Again causing the red end of the spectrum to fall upon the slit next the eye, I alter the width of that slit and find that narrowing it causes the distance between any two rectangles to increase, the rectangles themselves broadening out, whilst widening it causes it to decrease, the rectangles getting narrower and narrower, eventually meeting at the centre.

By experiments of this kind the wave length of light of any colour may be determined, and we must consequently devote some little time to studying the entire series of phenomena.

Let us imagine the second slit just filled by a single direct ether wave which has reached it from the first slit. Then every ether particle in the second slit becomes the centre of a series of secondary waves transmitted in all directions through the ether between the slit and the eye.

Let us suppose that the obliquity of certain of these secondary waves is such that they differ from each other by a whole wave length; when this is the case, evidently every wave on one side of the centre will find a wave on the other side in complete discordance with itself, and this state of things will cause the first dark band.

So that if we measure the angular distance between this band and the centre, and know the width of the slit, we are in possession of sufficient data to calculate the wave length of the light employed.

Thus, in fig. 5 let AB represent the slit, and CBD the obliquity of the first dark band. Then with A as centre and AB as radius, we draw the semi-circle EB, and from A draw AF at right angles to BC.

Then evidently BF is the wave length of the light employed.

Knowing  $AB$  = distance between jaws of slit and angle  $CBD$  = obliquity of first dark band, we can calculate the distance  $BF$ . For since angle  $CBD$  = angle  $FAB$ , the same relation will hold good between the length of the semi-circle  $EGB$  and the length of the portion of it  $BF$  as between the number of degrees included in the semi-circle (180) and the number included in the angle  $BAF$ .

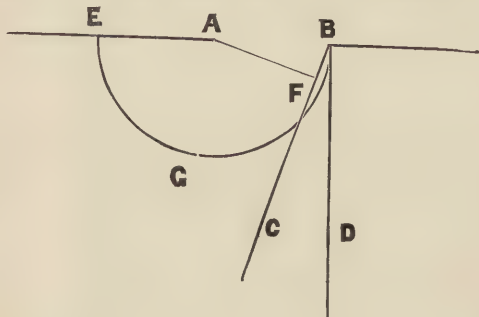


FIG. 5.—DETERMINATION OF THE WAVE LENGTH OF LIGHT.

And since the angle  $BAF$  is, as will be presently seen, a very small fraction of  $180^\circ$ , the curved portion of the circle  $BF$  may be taken as equal to the straight line  $BF$ .

In a particular instance it was found that with a slit  $\cdot 054$  inches wide or  $AB$ , the angular distance or  $BAF$  of the first dark band from the centre was  $1' 38'' = 98$  secs. Now a radius of  $\cdot 054$  inches corresponds to a diameter of  $\cdot 108$  inches, and this to a semi-circle of  $\frac{\cdot 108 \times 3.1416}{2} = \cdot 1696$  inches; and since in 180, the number of

degrees in the diameter, there are  $180 \times 60 \times 60 = 648,000$  seconds we get the proportion—

$$648,000 : 98 :: \cdot 1696 = \cdot 000026 \text{ inch.}$$

#### SUMMARY.

A musical chord is the result of aerial vibrations of various frequencies acting simultaneously on the ear, and prismatic analysis shows that white light is the result of ethereal vibrations of various frequencies acting simultaneously upon the eye.

When a syren is very slowly rotated, and the speed is then gradually increased, the notes first heard are due to aerial vibrations of lesser frequencies than those giving rise to the higher and higher notes heard as the speed of rotation increases.

Similarly, when an incandescent solid is gradually heated, the colours first perceived on viewing it through a prism are the result of ethereal vibrations of lesser frequencies than those which come into view as the temperature rises.

The *red* or *least refrangible* end of the spectrum is then due to *slower ethereal vibrations* than the *violet* or most refrangible end.

The distance from *crest to crest* or *trough to trough* of a wave is called the *wave length* (L).

The *velocity* of propagation of a wave (V) is the *time* taken for the wave to pass over a *certain distance*. This is commonly spoken of as the *velocity* of the sensation itself. The velocity of sound in air is 1,120 feet per second, that of light in air 186,000 miles per second.

*Sounds of all pitches, i.e., sounds due to aerial vibrations of all frequencies, are found to be propagated with the same velocity through air.* Since alterations in frequency of the particles in a wave makes no difference in the velocity with which the wave is transmitted, the *length* of the wave must vary as its frequency varies, *i.e., a small frequency must correspond to a long wave, a high frequency to a short one.*

Calling V the velocity of propagation of the wave, L the length of the wave, and F the frequency of the particles in it, then  $V = L F$ , a result true for light as well as for sound.

Particles moving in the same direction are in *similar phase*; particles moving in *opposite* direction in *dissimilar phase*.

In a row of particles evidently those which are 1, 2, 3, 4, 5, &c., wave lengths, or 2, 4, 6, 8, 10, &c., half wave lengths, from each other, will be in *similar phase*, and those 1, 3, 5, 7, 9, &c., half wave lengths from each other in *opposite phase*.

We cannot have two particles in *opposite phase* and vibrating with equal amplitude in the same plane, as they *destroy each other's motion*. This result is called *interference*. When it occurs with aerial particles giving rise to sound (*i.e., to a note of the same pitch*), *silence* is the result. When it occurs with ethereal particles giving rise to light (*i.e., to a colour of one degree of refrangibility*), *darkness* is the result.

If aerial or ethereal particles vibrated so as to produce only a series of waves radiating from the centre of disturbance, the ear or eye moved to the right or left at a certain distance from the centre of disturbance would appreciate *alternate sensations* of sound and silence and of light and darkness.

As no such result occurs we must look upon each particle of air or ether of the main wave propagated in a certain direction as being the centre of a series of secondary waves at all angles to that direction.

Some of these secondary waves must, and do, *destroy each other by interference*, but ordinarily the effect (silence or darkness) is *not apparent*, owing to the greater amplitude of every particle in the main wave.

If, however, in the case of light the greater part of the main wave is cut off by a narrow slit placed in front of a source of light of one degree of refrangibility, and this is viewed through another slit parallel to the first, some of the secondary waves emanating from

the second slit *interfere* and produce *darkness*, whilst others coalesce.

We see then a central bright image separated from one or a series of bright side images by dark spaces.

The angular distance between the first dark space and the centre of the field varies with the width of the slit next the eye. If this is narrow the displacement is great, whilst if wide the displacement is small, so that, knowing the width of the slit and the displacement of the first dark band, we can at once calculate the wave length of the light in question.



### LECTURE III.

THE SOLAR SPECTRUM—FRAUNHÖFER'S LINES AND THE WAVE LENGTHS AND FREQUENCIES CORRESPONDING TO THEM—EFFECT OF SOLAR SPECTRUM UPON SILVER BROMIDE—CURVES OF SENSITIVENESS OF SILVER BROMIDE, CHLORIDE AND IODIDE, AND THEIR DETERMINATION—PHYSICAL EXPLANATION OF COLOUR—USE OF RED LIGHT FOR DARK ROOM ILLUMINATION—PHYSICAL MEANING OF BLACK AND WHITE—ABSORPTION BY CERTAIN SUBSTANCES OF ENERGY POSSESSED BY MOVING PARTICLES OF AIR OR ETHER—WORK PERFORMED WHENEVER ENERGY IS ABSORBED.

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IT will be readily understood that the method applied in the last lecture to the measurement of the wave length of red light would also answer when applied to the measurement of the wave length of light of any other colour, the only modification necessary consisting in shifting the first slit until some other portion of the spectrum fell upon it. Since, however, each of the spectrum colours occupies a considerable space, which space, moreover, varies with the material of the prism employed, or with the method adopted to obtain the spectrum, we must select in making these measurements some point in each coloured band which shall always correspond to light of a definite degree of refrangibility.

Very fortunately such points occur in the solar spectrum. When this spectrum produced by any method is examined, each ray is seen to be traversed by a series of lines, called after their discoverer, Fraunhofer, which lines invariably occupy the same relative positions, and it is with reference to the most conspicuous of these lines lettered from A in the infra-red to H in the ultra-violet that wave lengths are actually measured. (See frontispiece.)

The latest determination of wave lengths is that made by Bell in 1888, and his values for the lines from A to E are given in the next table, together with the older values obtained by Angstrom for the lines from F to H, the values being given in fractions of an inch.

## ETHEREAL WAVE LENGTHS AND FREQUENCIES.

*Fraunhofer's Lines.**Wave Lengths.*

A	..	..	..	..	·00003000509470
B	..	..	..	..	·00002710274107
C	..	..	..	..	·00002583880659
D <sub>1</sub>	..	..	..	..	·00002321326066
D <sub>2</sub>	..	..	..	..	·00002318997961
E	..	..	..	..	·00002074456481
F	..	..	..	..	·00001913665464
G	..	..	..	..	·00001695764325
H <sub>1</sub>	..	..	..	..	·00001562205537
H <sub>2</sub>	..	..	..	..	·00001548422100

Knowing the wave length corresponding to any particular line, and taking the velocity of light as 186,000 miles per second, we can at once calculate the wave frequencies from the formula  $L = \frac{V}{F}$ .

To certain of these waves every substance employed in photography is sensitive; the action of white light upon such substances being due to the fact that in white light all these waves co-exist.

Let me take as an example of a sensitive substance silver bromide in gelatine in the condition in which it exists in a very rapid commercial dry plate.

Extinguishing all light but that emitted by my ruby lamp, I once more project the spectrum on the screen, and marking in pencil the position occupied by the extreme visible red, I cap my lens and place on the screen, in the position occupied by the spectrum, a narrow gelatine plate about twice as long as the visible spectrum, in such a way that one extremity of it, on which I have scratched a cross, is at the pencil marking, showing where the visible red ends.

Uncapping my lens, I expose the plate for half-a-minute in the spectrum, after which I again cap my lens and put the exposed plate in an ordinary developer containing alkaline pyro.

Looking at the plate I see that the darkening begins at a point about one-third the distance from one end, and the darkening is now gradually extending in both directions. The plate being completely developed, I wash it free from the developer and place it in its former position on the screen.

Once more removing my lantern cap, the spectrum falls above and below the darkened plate, and we are immediately made cognisant of the fact that the plate has darkened, or is sensitive not only to all the *visible* rays, but to others extending beyond the boundary of the violet.

A cursory examination shows, however, that the degree of darkening, or the thickness of the layer of dark-coloured product, is not the same everywhere, being greatest at the blue, and gradually shading off in both directions from this point.

Now, as you know very well, fixation does not remove the dark-coloured product, which, as a matter of fact, is metallic silver, so that it would be a very simple matter to fix the plate and estimate the quantity of silver present at various portions of it; or instead of doing this we might determine the visual opacity of the deposit by photometric methods (*vide* Lecture V.)

Let us suppose that in a square inch of the portion of the plate where the deposit was greatest we found by analysis one grain of silver, and that, having examined other portions at equal distances right and left from this, we noted the exact fractions of a grain of silver present, then we could obtain the curve of sensitiveness in the following way:—

Drawing a line we would begin by dividing it into any number of equal parts, and from each of these divisions we should draw a perpendicular, the height of which was proportional to the quantity of silver found at any particular spot. Supposing, for instance, we agreed to represent a deposit of one grain of silver by a perpendicular one inch in height, then a deposit of  $\frac{3}{4}$  grain would be represented by  $\frac{3}{4}$  inch, and so on. Connecting the summits of all these perpendiculars, we should obtain a curve such as that shown in the frontispiece, and on that curve it would be easy to localise the various Fraunhofer lines, if the experiment had been performed, as it should have been, with the solar spectrum.

Whilst I have been explaining the construction of this curve, my assistant has been exposing in the spectrum fresh strips of glass coated with silver chloride in gelatine and silver iodide in collodion.

Developing the first of these with ferrous-ammonium citrate, and the second with acidified pyro mixed with a little silver nitrate, and then, placing the developed plates in the spectrum in the position they occupied before development, you see that not only do the results differ from each other, but they also differ from that obtained with the silver bromide.

Just as before I could, by operating with the solar spectrum, obtain a fresh series of curves corresponding to the particular compounds in question, and the three curves would show at a glance the relative sensitiveness of the three compounds under the given conditions (see frontispiece). We learn from this that all rays have not the same effect upon silver bromide, chloride and iodide, although in the main we may say rays from the blue to the violet have the greatest effect, and those from the blue to the red the least.

You are, of course, aware that the light used for manipulating sensitive plates must be of a yellowish or reddish colour, and we learn the reason of this by placing a piece of ruby glass just in front of the prism, when all the rays but the red are seen to be cut out.

Now, since the red rays are, with silver bromide, least operative, and with silver chloride and iodide absolutely inoperative, we

naturally glaze the windows or other sources of light of our dark room with such glass, so that little or no light capable of affecting the sensitive substance can reach it.

Substituting for the ruby a piece of blue glass, you see that it transmits blue, green and violet, whilst a piece of violet glass transmits violet and a good deal of blue, the experiment of placing glass of any colour in the spectrum showing precisely what rays it transmits. The experiments with the blue and violet glass teach us that it by no means follows that the colour the unaided eye judges a sample of coloured glass to transmit is necessarily the only one it actually transmits. Our blue glass seemed blue to the eye, but the spectrum showed that it transmitted green and violet as well, and just as the unaided eye could not judge of the precise rays transmitted by this glass, neither could it judge of the precise rays transmitted by ruby glass.

Here I have another sample of ruby glass, and, placing it in the spectrum, you see that it transmits red, orange, yellow, and some green. Now, although to the naked eye this sample would seem as suitable as the former one for the windows of our dark room, the spectrum teaches us that this is not the case. But, of course, although the light transmitted by this sample would fog silver bromide, it would be quite safe for silver iodide, and comparatively safe for silver chloride.

Taking now my original piece of ruby glass, and interposing it in the path of the spectrum conjointly with the violet glass, you see that, although each separately would transmit certain rays, both combined transmit no light at all. The experiment teaches us that the rays which are not transmitted are not merely reflected off, as we might fancy, by the glass, but actually absorbed by it.

Violet glass absorbs red, and it is precisely because such rays only are transmitted by the ruby glass that both combined transmit no light.

We obtain results precisely analogous to these with reflected light. Placing this red ribbon across the spectrum, you see that in the red it appears red, whilst in the other spectrum colours it seems black, the reason being that the material absorbs these latter colours and reflects red only.

Substituting a blue ribbon for the red one, we get a different result, absorption now taking place in the red, and the other colours, particularly the blue, showing up more or less.

Placing a piece of black velvet in the spectrum, no colours are visible, all being absorbed, whilst the white paper screen, of course, reflects them all. (We put these results in scientific language by saying that black is due to the absorption of ethereal vibrations of every frequency, white to the non-absorption of ethereal vibrations of any frequency (at least, of those concerned in producing light), whilst colour is the result of a selective process, vibrations of certain frequencies being absorbed, and vibrations of other frequencies passing through or glancing off unchanged.)



We can obtain analogous results with these two tuning-forks which have been detached from their cases. Striking one of them against the table, and holding it in my fingers, no sound is heard, but if I press the extremity held in the fingers against this drawing-board, you hear at once a musical note.

Repeating the experiment with the other fork, a similar result is obtained.

The drawing-board here corresponds to a black surface, and the fingers to a white one. The fingers being incapable of taking up the vibrations of the tuning-fork, these consequently remain throughout of an amplitude too small to affect the ear.

The drawing-board, on the other hand, by absorbing the vibrations of smaller amplitude, converts them into vibrations of larger amplitude, sufficiently large, in fact, to render the ear cognisant of their existence.

I have here two glass jars of different heights, and holding one of the vibrating forks over the taller jar nothing is heard, but the sound becomes plainly audible when the fork is held over the second jar.

Substituting now the second fork for the first one, we find that holding it over the shorter jar causes it to be heard, whilst the taller jar exerts no influence upon it.

We have in the two forks the analogy of a blue ribbon held in the spectrum and absorbing red light, and of a red ribbon held in the spectrum and absorbing blue light.

But, you will say at once, the red ribbon appeared black in the spectrum blue, because it absorbed those particular rays—a result which should correspond rather to the suppression of the sound of a tuning fork than to its reinforcement.

But we must remember that in the spectrum we have a practically unlimited amount of energy emanating from the incandescent lime, whilst with the vibrating tuning fork the amount of energy is limited by the force of the blow given to it.

Now, although it is true that the *loudness* of the sound does increase for the time, the *duration* of the sound is actually shorter when the fork is held over the jar than when held in the hand.

To prove this I have two forks yielding the same note, and detached from their bases. Holding both in the right hand I strike the two sets of prongs simultaneously against the table, and I then place one of the forks over the resonant jar, keeping the other held at a distance in the fingers of the left hand. After a few moments our ears reveal the fact that the fork whose note we heard is at rest, but the other is still vibrating, as I prove by now placing it over the jar, when the note rings out quite loudly.

We learn, therefore, that the increased loudness of the note was really due to the absorption of a portion of the energy possessed by the fork, and therefore quite analogous to what occurs when a coloured ribbon absorbs certain spectrum rays.

Now since black absorbs all the spectrum rays we may reason-

ably ask ourselves what becomes of the comparatively large amount of energy which a black surface takes up.

To answer this question, I have a small incandescent lamp in a vessel of clear water containing a thermometer. First reading off the temperature of the water, which I find to be  $10^{\circ}$  C., I then cause the filament to glow by passing a current of electricity through it.

Three minutes having now elapsed, I again note the temperature of the water and find it to be  $12^{\circ}$  C. In three minutes then an amount of energy corresponding to a rise in temperature of  $2^{\circ}$  has been absorbed by the clear water.

I now pour some ordinary writing ink into the water so as to make it perfectly opaque, and three minutes having again elapsed I once more read off the temperature of the water, which I now find to be  $21^{\circ}$  C. In three minutes, then, an amount of energy corresponding to  $9^{\circ}$  has been absorbed by the opaque liquid.

What is the reason of the difference? Simply that the clear water absorbed comparatively little of the radiant energy given out by the glowing filament, because, being transparent most of that energy (at least that concerned in producing light) got through. But by rendering the water opaque I caused it to absorb the luminous as well as the other rays, and the greater amount of absorbed energy was represented by its correspondingly greater rise in temperature.

To illustrate still further this important point, I remove the lamp from the water, and, connecting one of its terminals to one terminal of a small electric motor, I connect the battery to the other motor terminal. On holding the motor shaft in the hand so as to prevent it from spinning round, you notice little or no diminution in the light, but on releasing the shaft so as to permit it to revolve, you notice that the glow of the lamp is greatly enfeebled.

When the motor was at rest the greater part of the energy supplied by the current was absorbed by the lamp and converted by it into light and heat, but when the motor was permitted to rotate some of that energy was absorbed by the motor with a corresponding diminution in the glow of the lamp.

Now we saw that pure red glass absorbs all the rays but the red, and it is easy to see that silver bromide, which is practically unacted upon by red, must also absorb somewhat similar rays. Viewed in the light of this explanation, we may, in fact, say that we glaze our dark room windows with ruby glass to enable them to absorb these rays, which, if transmitted, would be absorbed by the silver bromide and so act upon it.

We can still further illustrate this point in the following way:—Placing in the path of the spectrum a thin film of silver bromide in collodion, in which condition it is comparatively insensitive, you see that it transmits red rays, but substituting for this a thin film of silver bromide in gelatine, in its most sensitive condition, you see that the blue rays are transmitted.

Now, since the insensitive modification transmits red rays, it cannot, of course, absorb them, whilst these rays would be actually absorbed by the sensitive modification transmitting the blue rays. Hence the sensitiveness of the latter substance to the red end of the spectrum should be much greater than the former—a conclusion that is borne out by direct experiment.

We have seen that the absorption of energy means the performance of some kind of work. In the opaque mixture in which we placed our incandescent lamp the work was a rise in temperature; in our motor, motion; in our vibrating tuning fork, increased amplitude of vibration.

#### SUMMARY.

*Wave lengths, if determined for particular colours, would vary within certain limits owing to the difference in the spectrum produced by different means.*

A series of *dark lines* are always present in the solar spectrum, and always occupy the same *relative* positions. These lines, called from their discoverer, *Fraunhofer*, and lettered from A in the infra-red to H in the ultra-violet, are invariable *standards* for the measurement of *wave lengths*.

*Silver bromide* is sensitive not only to practically all the visible rays, but to certain others beyond the visible violet. Its actual sensitiveness is not the same at any two points, and this sensitiveness at any point can be determined by estimating either the amount of silver at that point in an exposed and developed plate, or by estimating its visual opacity. Either methods enable a *curve of sensitiveness* to be drawn.

This *curve of sensitiveness* varies for silver bromide, chloride and iodide, but, broadly speaking, those rays nearest the red are least operative, and those nearest the violet most operative, in producing change.

The colour of glass, seen by looking through it, or of a ribbon, etc., seen by looking at it, is determined by the transmitted or reflected rays.

White or transparency is the result of the reflexion or transmission of all colours, black or opacity the result of the reflexion or transmission of none, colour the result of a selective reflexion or transmission. The rays transmitted by any sample of glass for use in the windows, etc., of the dark room must be those which do not act upon the particular compound it is intended to employ.

The curve of sensitiveness of any compounds gives at once a means of selecting glass suitable for use with it.

Rays not transmitted by the (coloured) glass or the sensitive compound are absorbed.

Since energy is indestructible, its absorption must be accompanied by the performance of some kind of work, viz, a rise in temperature in the glass, chemical decomposition in the sensitive compound, &c.

## LECTURE IV.

REPRESENTATION OF DIRECTION OF A WAVE BY A STRAIGHT LINE—  
PARALLEL, DIVERGENT, AND CONVERGENT RAYS—RECTILINEAL  
PROPAGATION OF LIGHT—INVERSION OF IMAGES YIELDED BY SMALL  
APERTURES—DEFINITION OF SHARPNESS, AND ITS LIMITATIONS—  
DIAMETER OF MINIMUM CIRCLE OF CONFUSION AND ARC SUBTENDED  
BY IT—THE PINHOLE CAMERA—COLSON'S RESEARCHES—LIMITING  
DISTANCES IN PINHOLE PHOTOGRAPHY—DISTINCTION BETWEEN  
FREQUENCY AND AMPLITUDE OF A WAVE—LAW OF INVERSE SQUARES  
AND ITS MATHEMATICAL AND DIRECT PROOF.

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WE have already learnt that light is the result of exceedingly short waves or undulations succeeding each other with great rapidity.

Now clearly, since these waves are exceedingly short, we may without sensible error indicate their *direction* by a straight line, which will not differ to the naked eye from the sinuous one.

Such a line, which we must remember has no real existence, being a direction only, is called a ray of light, and a number of such rays constitute a pencil of light.

And again, although the ethereal waves take place in all directions, we agree when representing them on a flat surface to confine our attention to those in one plane only, viz, the plane of that surface, tacitly assuming that what is true of rays in that plane will be true of rays in any others.

We speak of rays as parallel if they are situated at equal distances from each other, and divergent or convergent if these distances are unequal, the latter terms having reference to the direction which the series of rays takes. Thus, a series of rays divergent if they proceed from a point would be convergent if moving towards that point.

We call a medium any substance such as air, water, glass, etc., into which light can penetrate, *i.e.*, in which the ether can vibrate. If this medium is chemically and physically the same throughout it is said to be homogeneous, if chemically or physically different heterogeneous.

In a homogeneous medium light is propagated in straight lines—a fact proved by the inversion of the image of objects on one side of a small hole, at the other side of which a screen is placed. Thus, in fig. 6, let A B represent two luminous points in front of H, a small hole in the shutter of a darkened room. Then of the rays diverging from A only those in the direction A A<sup>1</sup> can find admit-



tance, and the same is true of the rays diverging from B. Any single ray from A will then fall on a screen at  $A^1$ , and any single ray from B at  $B^1$ , and since a series of such rays give the image of the points the image  $A^1$  will be formed below  $B^1$ , although the point A is actually above B.

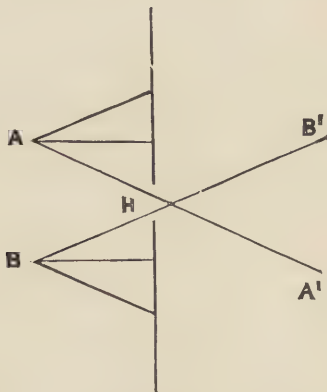


FIG. 6.—RECTILINEAL PROPAGATION OF LIGHT.

Now a luminous body is made up of an infinite number of points, and as each one of these would act just like the points A and B in the figure it is evident that the image should be inverted if rectilinear propagation is a fact, and since the image is inverted we have proof positive that light is actually propagated in straight lines.

The actual *size* of the image with reference to that of the object will depend purely upon the position of the screen, for evidently by moving this nearer to or further from the aperture the size of the image is decreased or increased. If the distance from object to hole is the same as that from screen to hole then the image will be of the same size as the object; if the object is nearer the image will be larger, if farther off smaller.

It is evident that if we took special precautions to exclude all light save that which passed through the hole a sensitive plate placed where the screen was would receive an impression, and we should have made, in fact, a pinhole negative, and as this is the simplest way to produce a negative we will consider it first.

We must begin with thoroughly understanding what is meant by the photographic term sharpness. Placing a slit about half-an-inch wide in front of the condenser of my lantern, I project the image of it on the screen as a narrow rectangle of light.



Focussing this slit so that the edges are what I would call sharp at my distance from the screen, you see that I can alter the position of the lens by a small amount without any loss in sharpness being perceptible.

A closer examination reveals the fact that, although no loss of sharpness occurs when the image is viewed at a certain distance, the loss of sharpness is very perceptible when that distance is decreased; the smaller the distance, in fact, between the eye and the image the lesser the amount of permissible motion of the lens.

Examining the image of the edges of the slit at the distance of 12 inches whilst my assistant racks the lens in and out by a small amount I see that, starting from the position of perfect sharpness, the racking out of the lens causes the distance between the edges of the image to increase, whilst the racking in of the lens causes that distance to decrease.

Now, causing the lens to be moved until the image just ceases to be sharp, I increase my distance to 24 inches, and find that the image, indistinct at 12 inches, is sharp at 24 inches. Again, causing the lens to be racked in until the image is just indistinct at 24 inches, I increase my distance to 48 inches, when the image again appears sharp.

Keeping now the distance between the eye and image constant, but varying the distance between the lens and the image, I first reduce this to 12 inches, and find that at that distance a very small amount of motion of the lens suffices to make the image indistinct, whilst if the distance from lens to image is increased to 24 inches a larger amount of motion is permissible.

Since, then, I can always cause the lens to be racked in or out by a small amount without altering the sharpness, I have in the altered dimensions of the image a means of expressing the permissible motion in terms of alteration in size of the image.

But since that amount of permissible motion, and the consequent enlargement or reduction of the image, depends upon the distance of the image from the lens, I must maintain this constant when measuring the altered dimensions of the image.

Substituting for the screen a plate of glass on which three lines are ruled  $\frac{1}{20}$  inch from each other, I place this 12 inches from the lens. Behind the plate is a small Ramsden eyepiece focussed on the lines, and placing my eye to it I rack my lantern lens in and out until the image is perfectly sharp, and then move the glass right and left until one edge of the image falls on the central line.

I now remove the eye from behind, and having placed a sheet of paper over the glass screen I view the image from the front at a distance of 12 inches, at the same time racking in the lens until the sharpness is just lost. Now removing the sheet of paper and applying my eye to the Ramsden eyepiece, I find that the edge of the image falls on the inner line. Again viewing the image from the front I rack out the lens until sharpness is again lost, and when this occurs examination from the back shows that the edge of the slit is now on the outer line.

Since the inner and outer lines are  $\frac{1}{100}$ th of an inch from each other, it follows that, considering the image of the edge itself as a line, any alterations in the width of a line falling within  $\frac{1}{100}$ th of an inch will not result in loss of sharpness when viewed at a distance of 12 inches.

Or, again, looking upon the intersection of two mathematical lines (length without width) as a mathematical point, we may say that an image is sharp if every mathematical point in it is expressed by a circle or disc of less than  $\frac{1}{100}$ th of an inch diameter.

This is called the limit of the *circle of confusion*.

Now, a circle  $\frac{1}{100}$ th of an inch viewed at a distance of 12 inches subtends an angle of one minute, and we may express the result more generally by saying that an image is sharp if when viewed from *any* distance, what should be a mathematical point in it subtends less than a minute of arc.

This shows, of course, that a photograph quite wanting in sharpness viewed from a certain distance is seen with satisfactory definition when that distance is increased—a result of everyday experience, and quite conformable to the scientific explanation just given.

Let us suppose now (see fig. 7) that in taking a pinhole photograph we have an aperture at *o* and an object at *ab*. Then the want of marginal sharpness in the image formed on a screen at any distances *x*, *x*<sup>2</sup>, *x*<sup>1</sup> between *oA*<sup>1</sup> is defined by the distance between the lines *ca*<sup>1</sup>, *c*<sup>2</sup>*a*<sup>2</sup>, *c*<sup>1</sup>*c*<sup>3</sup>.

Assuming that *ca*<sup>1</sup> is equal to the diameter of the circle of confusion, it follows, therefore, that the image sharp at *xy* would be no longer sharp at *x*<sup>1</sup>*y*<sup>1</sup>, i.e., with an object at a given distance the distance of the screen from the pinhole must not exceed a certain minimum.

If, however, the object was at *AB* then the want of marginal sharpness at *xy* would be *less* than before, and to get the *same* want of marginal sharpness the screen would have to be moved towards *A*<sup>1</sup>. Evidently, then, if *xy* is the *best* position of the screen with a near object, *ab* the best position with a more distant object will be further off.

In other words, as the distance of object from pinhole increases so must the distance from screen to pinhole increase.

Let us suppose next that the size of the aperture was diminished, the object being at *ab* and the screen at *xy*, then it is clear that to get a circle of confusion of the same diameter as before the screen would have again to be moved further off. Hence the smaller the pinhole the further the screen.

It might be thought at first sight that, the object being at *AB* and the screen at *x*<sup>1</sup>*y*<sup>1</sup>, the fact of bringing up the screen to *xy* would increase the sharpness by altering the diameters of the circles of confusion, and that the smaller the pinhole the smaller also would be the diameters of these circles.

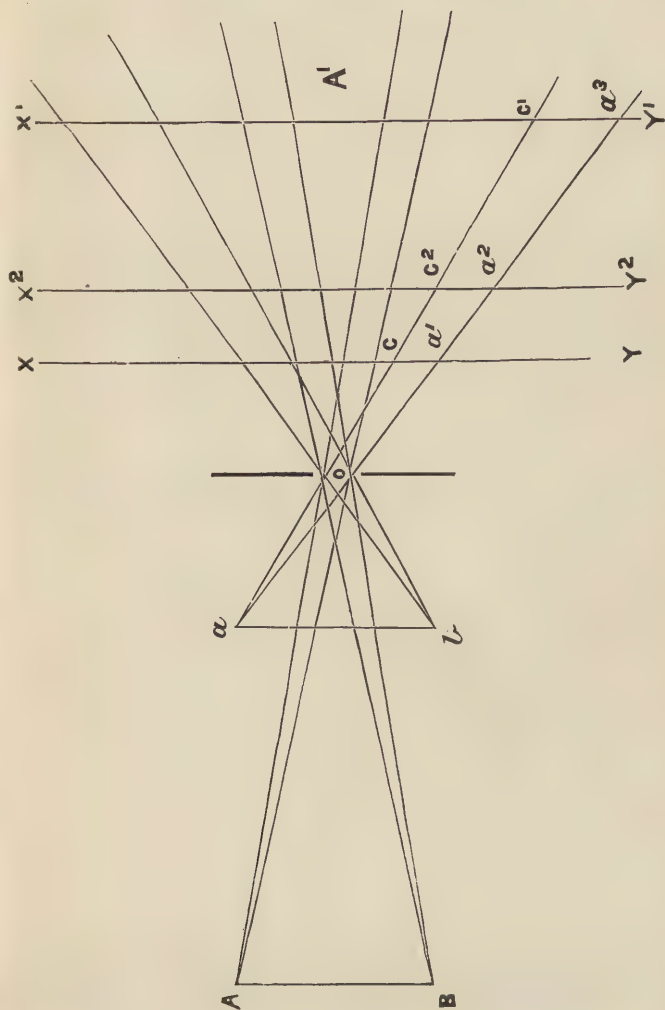


FIG. 7—PRINCIPLE OF PINHOLE PHOTOGRAPHY.

Both results are no doubt true in the abstract, but we must, in addition, consider the effect of interference (*vide* lect. ii.) Evidently if the obliquity of the marginal rays exceeds a certain amount this will occur, and as the obliquity increases, both by decreasing the distance of the screen from the pinhole and by decreasing the size of the latter, it is clear that there is a minimum distance and a minimum diameter.

We may then sum up by saying that with a pinhole of not less than a given size there is a minimum distance at which the screen must be placed, and that this distance in its turn regulates the distance at which the object must be.

It is not easy from purely theoretical considerations to trace out the relation between the size of the pinhole and the two distances, but the French physicist Colson has made a most elaborate series of practical experiments with plates and objects at different distances from pinholes of various sizes, and finds that to get the greatest possible sharpness the distance  $D$  of the object, that  $d$  of the plate, and the diameter  $a$  of the pinhole must be so connected that

$$d = \frac{a^2}{\cdot 00081 - a^2} D$$

And from this formula, arrived at from direct experiments, the following table has been calculated, in which are given the distances and apertures corresponding to each other, distances and diameters being expressed in inches.

COLSON'S TABLE FOR PINHOLE APERTURES.

Distance of Object from Pinhole.	Distance of Plate from Pinhole.	Diameter of Pinhole.
5.2	2.0	·0080
18.0	4.4	·0120
40.0	8.0	·016
80.0	12.0	·020
132.0	17.6	·024
197.0	24.4	·028
248.0	32.0	·032
450.0	40.0	·036
604.0	49.2	·040

A ray emitted from a luminous source is, as we have seen, the representation of the direction of the wave travelling from that source to, say, a screen placed at a certain distance from it. Let us suppose that the luminous source is a piece of red glass

placed quite close to this large and broad gas flame. Then the eye, situated at any reasonable distance in front of the red glass, will receive the impression of red light, and since this is the result of waves of a certain definite length and frequency, it follows that these waves are of the same length and frequency whatever their distance from the source may be.

But it is also evident that, although the colour is the same at all distances consistent with visibility, the intensity or brilliancy of the light varies very considerably, becoming more and more feeble as the distance increases.

Now, just as the length of the wave determines the colour, so its amplitude, which we remember is the distance through which each particle moves, determines the intensity, the law being that this varies inversely as the square of the distance of the body illuminated or acted upon from the source of light, a law which holds good with every form of radiant energy, due to vibrations occurring through ether, air or any other substance.

You will remember the intimate connection that exists between light and heat, and from which we are led to conclude that heat, like light, is the result of ethereal vibrations. Now, if the law stated above is true for light, it must also be true for heat, and that it is true for heat I prove in the following direct way.

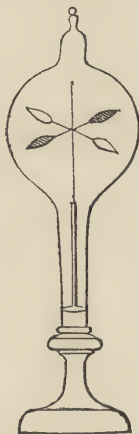


FIG. 8.—THE RADIOMETER.

Placing my radiometer (fig. 8) at two inches from this gas flame you see the vanes are revolving. Without for the moment pausing to inquire into the exact reason of the motion, we may at



all events satisfy ourselves that it is due to the absorption of energy of some kind by placing a vessel of clear water between the instrument and the flame, when the motion becomes slower and slower, and finally ceases.

Removing now the vessel of water, I permit the vanes to rotate, and when they have reached their maximum velocity I will count the number of times one particular vane revolves in one minute. Doing this, I find that the vane goes round 50 times. Removing now the instrument to four inches from the flame, I repeat the experiment, and now find that in a minute the vanes go round 12 times. Now the square root of 50 is a little over 7, and the square root of 12 is nearly 3·4, numbers which are practically in the ratio of 2 to 1, thus proving that the energy absorbed at unit distance was four times that absorbed at twice that distance.

To prove the truth of the law in the case of light, I alter the position of the incandescent lime in any lantern so that the condenser emits parallel rays, and then remove the front lens. Placing now a square of ruby glass over the front of the condenser I cause all the lights to be extinguished, and this done I put at one foot from the condenser this slide containing a sensitive plate. The slide is made, as you see, with two shutters opening from the centre so that we can give the two halves of the plate independent exposures. Opening the shutter to the right, I remove the ruby glass and expose the half-plate for three seconds to the light. Replacing the ruby glass I place the slide two feet from the condenser, and opening the other shutter and closing the first I remove the ruby glass and give this half an exposure of twelve seconds. Once more replacing the ruby glass I plunge the entire plate into an ordinary alkaline developer, and after three minutes therein I remove and fix it, when, on passing it through the lantern, you can detect no practical difference in intensity between the two halves. But since the half at unit distance received only one quarter the exposure of the other half at twice that distance, we see at once that the law is true for light as well as heat, viz., that the intensity varies inversely as the square of the distance of the body illuminated or acted upon from the source.

#### SUMMARY.

*A wave which we believe to really exist is represented in direction by a straight line called a ray.*

*Rays are either parallel, convergent or divergent.*

*An object which is really a series of fine reflecting points forms an inverted image on a screen placed behind a small aperture, and from this we conclude that rays of light are not bent, i.e., that light is propagated in straight lines.*

*The image of an object also consists of very fine points.*

*If these are circles instead of points their size determines the want of sharpness of the image.*

The eye placed 12 inches distant from a circle  $\frac{1}{100}$  inch in diameter sees it as a point, hence if the image of what should be points are circles of equal or less diameter than this we call the image sharp.

A circle  $\frac{1}{100}$ th inch diameter subtends an arc of one minute, hence, expressing the maximum diameter of the circle of confusion in angular measure, we avoid the necessity of restricting ourselves as to what distance it is to be viewed at. In images formed by pinholes the larger the pinhole the greater the diameter of the circle of confusion. Decreasing the size of the pinhole increases therefore the sharpness up to the point when interference comes into play, so that we cannot decrease the size of the pinhole indefinitely.

Increasing the distance of the image from the pinhole decreases the sharpness, hence the further off the image the smaller the pinhole must be. But here again, since interference limits the size of the pinhole, we cannot increase the distance indefinitely.

Colour is independent of distance, but intensity is not.

Colour is the result of vibrations of definite frequency, changes in intensity (or brightness) the result of changes of amplitude.

The radiometer proves this law of inverse squares to hold good with heat waves due to vibrations of small frequency, and the amount of silver on the two halves of the same plate which have respectively received exposures in the ratios of 4 and 1, at distances 2 and 1, proves it to be true with light waves of high frequency.

The intensity of illumination of any surface varies inversely as the square of its distance from the source of light.

## LECTURE V.

APPLICATIONS OF THE LAW OF INVERSE SQUARES IN CALCULATING  
EXPOSURES NECESSARY FOR CONTACT PRINTING AT DIFFERENT  
DISTANCES FROM A SOURCE OF LIGHT—CALCULATION OF EXPOSURES  
NECESSARY WITH LENSES—ADVANTAGES AND DISADVANTAGES OF  
SHORT FOCUS LENSES—RATIO BETWEEN DIAMETERS AND AREAS  
OF CIRCLES—CALCULATION OF EXPOSURES WITH LENSES OF THE  
SINGLE AND DOUBLE TYPE—MEANING OF RATIO OF FOCUS TO  
APERTURE—UNIFORM SYSTEM OF STOP NOTATION—PHOTOMETERS  
AND THEIR USES.

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WE have already learnt that the intensity of illumination varies inversely as the square of the distance of the illuminated body from the source of light, and we must now learn the bearing of this law on the important question of exposure.

Confining our attention for the moment to a sensitive surface of silver bromide which is exposed to light with the object of subsequently developing up an image upon it, it is well known that under given conditions a certain exposure, and that only, will give the best results.

Let us suppose that we are making contact prints on bromide paper, and find that at, say, one foot in front of a source of light an exposure of 12 secs. is requisite. Then, if we increase that distance to two feet, we should have to give an exposure of 48 secs., and at six inches an exposure of 3 secs. Practically, however, the law holds absolutely true only when the dimensions of the source of light equal the illuminated surface, or when the distance of the latter from the source is comparatively great.

In the case in point, using, say, a  $\frac{1}{4}$  negative and a small gas flame, the exposure at six inches would be found somewhat greater than that calculated out, and the exposure at 24 inches somewhat smaller owing to the greater and lesser obliquity of the light at the two distances as compared with its obliquity at 12 inches.

If, instead of making contact bromide prints, we were making pinhole negatives, then the law would also apply. Let us suppose, for instance, that the plate being eight inches distant from the aperture an exposure of 60 seconds was found to give the best result, then on increasing the distance to 12 inches the exposure would become

$$\frac{60 \times 12^2}{8^2} = 135 \text{ seconds.}$$

Were we employing a lens instead of a pinhole, the further off the object the nearer the plate, and the latter distance measured

from what is termed the back nodal point of the lens would enable the correct exposures to be ascertained.

Let us suppose, for instance, that in a particular case this distance was found to be 24 inches, the correct exposure being four seconds. Then, if that distance was reduced to 12 inches, the exposure would now become  $\frac{4 \times 12^2}{24^2} = 1$  sec.

With pinhole or lens, as with contact printing, the actual exposures at the shorter distances would be rather greater than the calculated ones, and rather smaller at the greater distance, owing to the fact that the rays are divergent and not parallel.

In the case of lenses, instead of measuring the distance from back nodal point to ground glass, it is less troublesome in many cases to estimate by the eye the distance of the object from the camera.

Now, in every case, the two corresponding distances, called respectively the major and minor conjugate foci, are such that their product divided by their sum equals the focal length of the lens, or, calling this latter  $F$  and the two conjugate foci  $f$  and  $f_1$ , then in every case  $F = \frac{ff_1}{f + f_1}$ .

And from this we see at once that, knowing the major conjugate foci in any two cases, the ratio between the two exposures is inversely as  $\left(\frac{Ff}{f - F}\right)^2$

It is evident that the greater the major conjugate focus is made the less the difference between  $Ff$  and  $F - f$ ; hence with every lens a point is reached at which this difference becomes negligible, and beyond that point distance ceases to have any further influence on exposure; and clearly the shorter the focus of the lens the sooner will this distance be reached.

We put the matter into practical language by saying that if the distance of the object exceed ten times the focal length of the lens, any further variation exerts no influence on the time of exposure.

If we compare two lenses of different foci, evidently that one which possesses the shorter focus will be the more rapid, since it will form an image at the shorter distance from the ground glass.

This gain in rapidity is, however, more than counterbalanced by the inequality of illumination given by lenses of very short focus. Let  $A$  and  $B$  (fig. 9) represent two lenses forming images at  $C D$ . Then the  $B E$ ,  $A E$  will represent the relative axial illumination, and  $B C$ ,  $A C$  the relative marginal illumination. Clearly, as  $A C$  becomes smaller and smaller,  $A C$  becomes correspondingly larger; hence, when  $A C$  very much exceeds  $A E$ , an evenly-exposed negative becomes an impossibility. It can easily be shown, for instance, that if a lens includes an angle of  $90^\circ$  the illumination at the margins is less than half that at the centre.

Since, however, such lenses must be used under certain circumstances, various devices have been proposed to remedy this inequality, one of the simplest of which consists of a disc of blackened cardboard, with radial slits caused to revolve immediately in front of the lens.

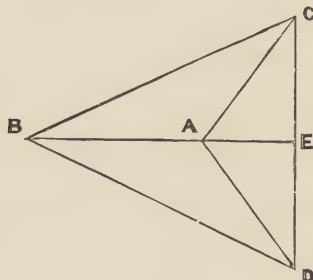


FIG. 9.—UNEQUAL ILLUMINATION GIVEN BY SHORT FOCUS LENSES.

It will be convenient at this point to consider the influence of the diameter of the stop upon the exposure. Taking first the case of a single lens of the so-called landscape type, with the stops placed in front, it is evident that since we may look upon the stop as an opening placed in front of the lens and regulating by its area the quantity of light which passes through, or the intensity of illumination, the greater the area the greater will be the intensity, and *vice versa*. Now as the duration of exposure varies inversely as the intensity, it follows that the duration of exposure will also vary inversely as the area.

Stops being circular in form, we have then merely to ascertain the relative areas of two stops, which areas inverted give the ratio between the exposures needed with the two stops. Since the areas of circles are proportional to the squares of their diameters, it follows, therefore, that the ratio between the two exposures is given by the reciprocals of the figures expressing the squares of the two diameters.

Taking, for instance, stops of  $\frac{1}{4}$  and 1 inch in diameter, the squares of these figures are  $\frac{1}{16}$  and 1, and their reciprocals 16 and 1 give the relative exposures.

With lens of the double form, such as rectilinears, Euryscopes, portrait lenses, &c., in which the stop is placed *between* two lenses, the matter is not quite so simple, for the rays falling upon the stop are no longer parallel, but convergent.

Let fig. 10 represent two such lenses with a stop placed between them at S S<sup>1</sup>. Now, as we shall see later on, the focal length of a lens is the distance measured from the centre of a plane A A<sup>1</sup>,



which, with the lens in question, is between the lens and stop, and the centre of another plane  $ff^1$  further behind the lens on which the image of objects situated at infinity is formed.

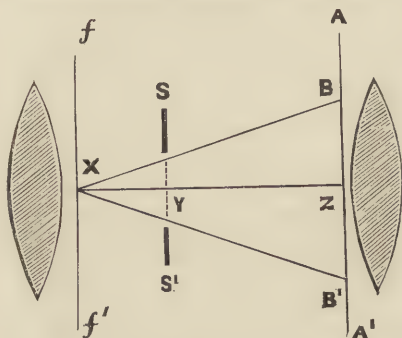


FIG. 10.—INFLUENCE OF DIAMETER OF STOP UPON EFFECTIVE APERTURE OF CERTAIN LENSES.

We may, therefore, look upon parallel rays passing through the front lens as converging from the points  $B B^1$  on the plane  $A A^1$  to the centre  $X$  of the plane  $ff^1$ . Clearly, therefore, a stop of the diameter indicated placed as shown would permit as much light to pass as a stop of the diameter  $B B^1$  if the front lens was removed.

Now it is easy to see that the diameter of the stop  $S S^1$  is to  $B B^1$  as the distance  $X Y$  is to  $X Z$ . The distance  $X Z$  is the principal focal length of the front lens which we call  $F$ , and the distance  $X Y$  is evidently  $X Z$  or  $F - Y Z$ . Calling this latter distance, viz., that between the stop and the nodal point of emission of the front lens,  $D$ , we see that  $X Z = F - D$ .

Now since the stop of the given diameter placed at  $S S^1$  admits under the given conditions as much light as a stop of a diameter equal to  $B B^1$  if the front lens was not there, if we call the *actual* measured diameter of this smaller stop  $A$ , the actual amount of

light admitted  $A$  is, of course, given by  $A = \frac{F A}{F - D}$

To prove the first of these points, I again render the rays from my lantern parallel, and having removed the front lens, I place the red glass over the condenser. Now placing in front of the red glass a piece of blackened card, with a hole one inch square cut in it, I expose half the plate to the cone of rays for five seconds by removing the red glass. Replacing now the red glass I substitute for the first piece of cardboard another with a hole half inch square cut in it, and expose the second half of the plate for twenty seconds.

On developing up the plate, fixing it, and passing it through the lantern, you will notice that there is no practical difference between the two halves, thus proving the truth of the first part of the law.

Replacing now the ordinary lantern lens I stop it down to one inch, and expose half of another plate in front of it for ten seconds. Substituting for this stop one half an inch in diameter, I give the second half of the plate an exposure of forty seconds, marking this half with a pin scratch.

Developing this plate and fixing it, I pass it through the lantern, and you see that the half marked with the pin scratch is notably denser than the other, showing that more light actually passed through the half inch stop than calculation would have led us to suppose.

The diameters of the stops supplied with a lens are commonly expressed as fractions of its focal length, the lens being said to be working at  $f/5$ ,  $f/10$ , &c. Thus, a lens working at  $f/10$  means one in which the focal length is ten times the diameter of the particular stop used, and clearly all lenses of *similar type* in which this *ratio* is maintained will be of the same rapidity whatever the actual focus or diameter of the top may be, and since the rapidities of two lenses vary inversely as the squares of the diameters of their stops and directly as the squares of their focal lengths, the rapidity ratios will be inversely proportional to the squares of the denominators of the fractions expressed in the usual way, and the exposure ratio directly proportional to the same figures.

Since we shall see further on that the diameter of the stop used with any lens varies on different occasions, it would obviously be a great convenience to have the diameters of all stops used with lenses of all foci so arranged as to give corresponding exposure ratios, and it would be a further convenience if the ratios between the exposures themselves were a comparatively simple one. Most good makers, following the example set by Dallmeyer, actually carry out this principle, and it may be well to explain the reasoning adopted to arrive at the requisite ratios of focus to aperture.

Since the squares of the usual ratios represent relative exposures it follows that the square roots of a series of exposures represented by, say, 10, 20, 30, 40, etc., would give what is required.

Now in practice it is found that for all photographic lenses the usual ratios fall between  $f/2$  and  $f/64$ , and the question is to find a series of numbers in comparatively simple ratios to each other whose square roots shall fall between these limits and so get the data enabling a sufficient number of stops to be cut for each lens.

Now it is easy to see that  $\sqrt{5}$  gives practically 2 and  $\sqrt{4000}$  practically 64, so that our exposure ratios must lie between 5 and 4000, and practically it is found that the square roots series 5,  $7\frac{1}{2}$ , 10, 15, 20, 25, 30, 40, 50, 75, 100, 150, 200, 250, 300, 400, 500, 750, 1000, 1500, 2000, 2500, 3000, 4000, give ratios which meet every requirement.

On this "uniform" system it is plain that an exposure once

found with any lens and any stop is found for every lens and every stop by the simple process of squaring the denominator of the fraction engraved on the two stops, and finding the simplest ratio between the figures (which must be two of those given above) so obtained.

The law of inverse squares finds an important application in photometers, or instruments for measuring the intensity of any source of light.

The simplest of these is the Rumford or Shadow Photometer, and the principle upon which it depends I can illustrate in the following way. Causing this candle flame to illuminate this sheet of white paper behind it, I place an opaque rod between the candle and paper, and at a short distance from the latter, so as to cast a shadow on the paper.

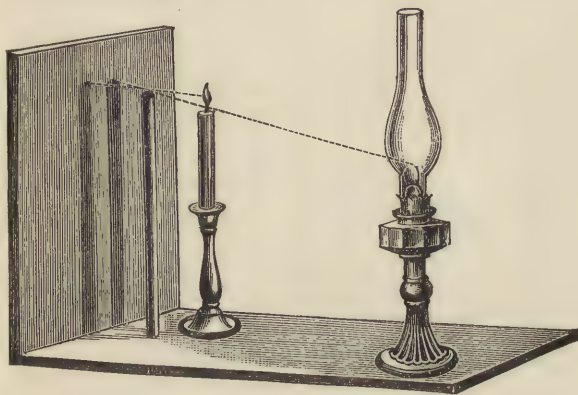


FIG. II.—THE SHADOW PHOTOMETER.

Now moving the candle further off you see that the blackness of the shadow has apparently decreased, whilst bringing it nearer causes the blackness to apparently increase (fig. 11).

Of course the opaque rod intercepts the light in every case, whatever, within reasonable limits, may be the distance of the candle from the screen, the apparent alteration in the blackness of the shadow being really due to the contrast between a shadow of fairly uniform blackness and white paper illuminated to different degrees.

It follows, therefore, that if two lights of different intensities are placed at unequal distances of the screen, and so arranged as to cast two shadows, we can, by decreasing the distance of the feebler

light from the screen, match the blackness of the shadow it yields with that of the shadow yielded by the other light, and evidently when we have done this the proportionate intensity between the two lights will be represented by the inverse squares of their respective distances from the screen.

It must not be forgotten, however, that such an arrangement measures the *luminosity* and not the effect of the light upon any particular sensitive substance. The method is occasionally useful to measure the relative luminosities of two lantern lamps, etc., but in carrying it out care must be taken that the distance from each light to screen is measured along a line drawn from that light to the shadow it casts.

If the two lights are at very different temperatures it will be found impossible to match their intensities by the naked eye. Thus using my lantern and a single candle I find that no matter how far away the limelight and how near the candle, the shadows cannot be made of equal blackness. If, however, I look at the shadows through either green or red glass I find that I can match them very readily, but the shadows brought to nearly equal intensity with the naked eye are no longer of the same intensity when viewed through the red glass, and if they are brought to equal intensity, using the red glass, this intensity will again alter when the green glass is substituted for it.

As a matter of fact, the hotter light appears brighter in proportion when viewed through the green than through the red glass, but by making a pair of observations first through green and then through red glass, the mean of the observed results will give what is required.

By an adaptation of this photometric method the visual opacity of the deposit at any portion of a sensitive plate can be measured.

Here, for instance, I have two rather narrow slits placed in front of two candles, at one foot from the screen, and under these circumstances both candles cast shadows of equal intensities.

If, however, I place behind one of the slits a sensitive plate, which has been exposed in the spectrum, and then developed, fixed and washed, the opacity of the deposit at that portion of it which is behind the slit causes the blackness of the shadow to diminish, but I can again match the blackness of the shadow by moving off the other candle to a greater distance. Measuring now this distance, which I find to be 51 inches, I slide forward the plate so that a fresh portion of it falls over the slit. The opacity at this portion is, as you see, less than that at the former portion, for the blackness of the shadow has increased, and to match it I must move forward the second candle to 47 inches. Now, evidently, the visual opacity at the two places will vary inversely as these two distances, or calling the visual opacity matched by the candle at 51 inches unity, then that matched by the candle at 47 inches will be  $\frac{51^2}{47^2} = 1.17$ .



## SUMMARY.

Since the *intensity* of light at distances 1, 2, 3, 4,  $n$ , &c., from the source varies as  $1, \frac{1}{4}, \frac{1}{9}, \frac{1}{16}, \frac{1}{n^2}$ , the *exposures* at these distances will be 1, 4, 9, 16,  $n^2$ .

This law holds good with contact printing and with pinhole and lens negatives.

With a lens the distance is reckoned not from the plate to the lens, but from the plate to the nodal point of emission of the lens.

Knowing the focus  $F$  of any lens and the distance  $f$  of the ground glass from the nodal point of emission, the distance  $f_1$  of the object from the nodal point of admission can be calculated from

$F = \frac{ff_1}{f+f_1}$  a relation which always holds true, hence relative exposures can always be calculated if we know  $F$  and either  $f$  or  $f_1$ .

The areas of circular apertures are proportional to the squares of their respective diameters, hence the exposures are inversely proportional to the squares of such diameters. If the apertures are in front of the lens no correction is necessary; if between two lenses a correction must be made, owing to the fact that the front lens renders parallel rays convergent.

The diameters of the stops supplied with lenses are commonly expressed as ratios of the focal length of the lens, i.e.,  $f/4, f/10$ , &c. Hence all lenses working at the same ratio of focus to aperture are of equal rapidity.

If ratios such as  $f/4, f/5, f/6$ , etc., are chosen, there is no simple ratio between the square roots of these figures representing the comparative exposures.

A series of numbers lying between 5 and 4000 can, however, be found in simple ratio to each other, and whose square roots give ratios suitable for all and every lens. This constitutes the "Uniform" system of stop notation.

A photometer enables the visual intensities of two sources of light to be compared.

In its simplest form it consists of an opaque rod very close to a white screen. When the blackness of the shadow cast by a brilliant light at a considerable distance is the same as that cast by a less brilliant light at a shorter distance the intensities of the two lights are inversely proportional to the squares of their distances from the screen.



## LECTURE VI.

REFLEXION OF LIGHT AND ITS LAWS—REGULAR REFLEXION—FORMATION OF IMAGES IN PLANE MIRRORS—LATERAL INVERSION—USE OF MIRRORS TO PRODUCE REVERSED NEGATIVES—HALATION AND ITS CAUSE AND CURE—THE PHILOSOPHY OF THICK FILMS—IRREGULAR REFLEXION—SCATTERED LIGHT AND ITS ADVANTAGES AND DISADVANTAGES—REDUCTION OF REGULAR REFLEXION FROM A SURFACE BY DULLING IT—PRACTICAL APPLICATION OF THIS.

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BILLIARD players well know that a ball caused to strike the cushions of the billiard table at a certain angle will rebound in a direction which can be readily predicted, the original direction being, in fact, related to the new one by a very

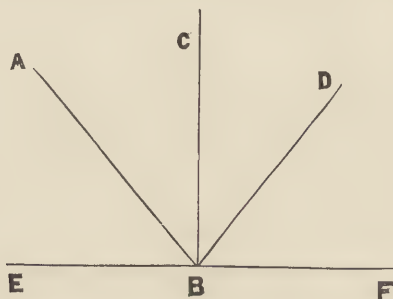


FIG. 12.—THE REFLEXION OF A WAVE.

simple law. Calling E F (in fig. 12) the cushion and A B the original direction, then the new direction B D will be such that the angles A B C and C B D are equal.

What is true of a billiard ball is equally true of a ray of light. Causing a beam (fig. 13) of light from my lantern to assume the direction L M, the light is reflected from the surface of the mirror at M, and holding a piece of smouldering brown paper in the beam you see the reflected ray takes the direction M R, such that the angles L M O and R M O both equal  $50^{\circ}$ .

Altering the direction of the mirror, I cause the ray L M to make a greater angle and you see that H M follows suit.

This important law of reflexion may be stated thus:—

Whenever light is reflected from an object the angle of incidence equals the angle of reflexion, both angles being measured from a perpendicular let fall upon the surface at the point where the incident ray meets it.

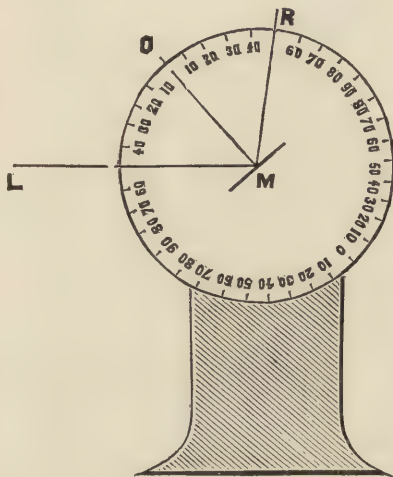


FIG. 13.—APPARATUS FOR ILLUSTRATING THE LAWS OF REFLEXION.

Now it is easy to see that if in fig. 13 the eye had been placed at R, L being a point of light, it would see that point as if it was situated in the line R M, the apparent distance of the point behind the mirror being equal to its real distance in front of it.

For if in fig. 14 P represents the point and M N the mirror, then any two rays P M, P N will take after reflexion the directions M M<sup>1</sup>, N N<sup>1</sup>, and the prolongations of such rays meeting *in imagination* behind the mirror give us the image of P at P<sup>1</sup>, and since the triangles O P N and O P<sup>1</sup> N are similar and equal, it follows that O P = P<sup>1</sup>.

Adjusting this silvered mirror so as to make an angle with the axis of my lantern condenser, some of you in front will see a luminous arrow, the reflexion of an aperture in the shape of an arrow placed just in front of the condenser.

Let us trace out what actually occurs in this case. The luminous arrow, or its image, being really an assemblage of luminous points, we will confine ourselves to two points at the extremities only. Calling the extremities of the arrow A B (fig. 15

then an eye placed at E will see the image at  $a\ b$ ,  $a$  and  $b$  being apparently as much behind the mirror  $M\ m$  as  $A$  and  $B$  are actually in front of it.

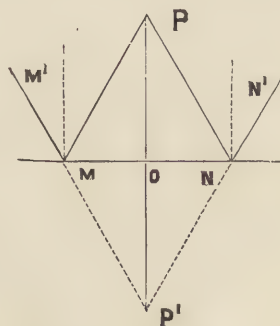


FIG. 14.—FORMATION OF AN IMAGE IN A MIRROR.

It follows at once from an inspection of the figure that the image must be laterally inverted, for in the arrow itself the head points *towards* an observer at E, whilst in the image the head points *from* him.

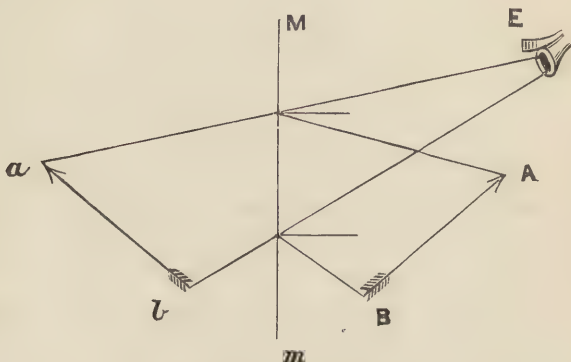


FIG. 15.—LATERAL INVERSION.

Now although we have called the representation of the arrow behind the mirror an image, it is not one in the same sense as that depicted on the ground glass of the camera.

Images formed on the ground glass of the camera are due, as we shall subsequently see, to the *intersection* of various rays proceeding in different directions from the same point of the object depicted, and such images are called *real*.

Now with a mirror it is easy to see that no rays proceeding from the same point, being divergent, can ever intersect in front of the mirror; but the imaginary production of these rays will intersect *behind* the mirror, for which reason the image is said to be a virtual one.

Lateral inversion occurs in positives viewed from the front and in negatives taken direct, but a positive or negative viewed from the back, or a negative printed from the front by any but the single transfer carbon process, gives, of course, images which are not laterally inverted.

Since a mirror laterally inverts, such a mirror placed at an angle of  $45^\circ$  in front of the lens will give a positive or negative which, viewed from the front, is not laterally inverted, or a negative which, printed from the front by any process but the one mentioned, gives a print which is laterally inverted. If, however, a print is made by single transfer in carbon then the positive, which would be laterally inverted if made from an ordinary negative, is now no longer laterally inverted, and the negative necessary to obtain this result is said to be "reversed."

Evidently if, in making the negative, we had caused the glass instead of the coated surface to face the lens, the negative would also be reversed, and a right-angled prism used instead of the mirror will, as we shall subsequently see, give the same result.

If, again, instead of a thick glass plate, which on account of its thickness can be printed from one side only, we had used a very thin celluloid support capable of being printed from either side, then we would have a negative reversed or not, according to the side turned towards the paper, etc., on which the print was being made.

In negative making it frequently occurs that what should be a very dense portion of the negative in close contact with a part of much smaller density is rendered as a gradual merging of the more dense into the less dense portion.

This results in the print in a gradual shading of the edges of the high lights into the shadows, the high lights being, in fact, surrounded by a halo from which effect the phenomenon is termed *halation* or *blurring*.

Projecting on the screen this transparency of a church interior you see around the central window a halo of light. What is the cause of this?

In the fig. 16 let O be a particle of silver bromide, portion, in fact, of the sensitive film P Q R S, spread on the glass plate Q S T U, and let rays B C meet this particle in a direction at right angles to the surface of the sensitive coating. Under these circumstances, B is reflected towards B<sup>1</sup> and alters any other par-

ticles in its path, but C reflected towards  $C^1$  alters any particles between C and  $C^1$ , and then entering the glass is reflected from its back surface towards H N. Evidently this ray will affect any particles between  $N^1$  N.

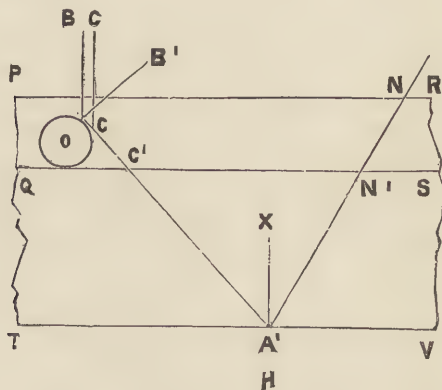


FIG. 16.—THE CAUSE OF HALATION.

Now the quantity of light reflected from T U is greatest when  $C^1$  H X equals a certain angle, and it follows that the sensitive film receives by reflexion an amount of light, very feeble, in the neighbourhood of  $C^1$ , then gradually increasing and finally gradually diminishing in amount.

Evidently the more transparent the sensitive film the less will it tend to scatter the light falling upon it, and if it could be made quite transparent no halation would occur.

But as matters actually stand the sensitive film is always more or less translucent, with the result that halation is always present. Clearly, however, the more translucent it is the less light it scatters, and it is partly for this reason that a gelatino-bromide plate shows halation to a more marked degree than a collodion one.

But we have also to consider the colour of the film, or, more precisely, the exact nature of the rays which it reflects. If these, as with a wet collodion or slow gelatino-bromide plate, are such (red rays) as act feebly upon it, then halation will be at a minimum; if, as with a very rapid gelatino-bromide plate, the reflected (blue) rays are such as act energetically upon it, then halation will be at a maximum.

It is evident that the thicker the layer of sensitive material the greater will be the amount of energy it can absorb, and the less consequently the halation, until with a certain thickness no



practical difference in the brightness of two overlapping images can bring about the result, and this forms a very cogent argument in favour of thickly-coated plates.

With regard to this halation it must be remembered that, with a comparatively thinly-coated gelatino-bromide plate, it must be present to a *certain degree* in every case where the amount of light reflected from two neighbouring points of the object differs in the slightest degree, and although plainly visible in certain cases, only such as in that just cited, it must, if present at all, result in a blurring of outline, and consequent loss of sharpness.

Even with thinly-coated plates there are, however, several other partial remedies for this evil.

A black surface will, as you know, absorb practically all light-producing waves, and a red one will absorb all, or nearly all, the waves acting upon silver bromide. If then we coat the back of the plate with a black or pure red substance, or, better still, interpose a layer of it between the back of the film and the front surface of the glass, we diminish halation.

Unfortunately, the interposition of any such substance between the front of the glass and the back of the film presents considerable though not insurmountable difficulties, for we must remember that the coating has to be removed before the negative can be printed from.

Coating the back of the plate, or "backing" it, as it is called, is, however, practicable, the removal of the backing after exposure and before development being quite easy.

Although, at first sight, the backing of a glass plate, or the employment of a very thin one of celluloid (in which case the reflected rays follow practically their original direction), would seem a perfect cure, yet this is not really the case. For although the reflection from the back of the glass is stopped, nevertheless reflection can still take place from the front of it. The only real cure consists either in making the layer of sensitive material sufficiently thick, or in placing the backing, not at the back of the support, but at the back of the film itself.

As illustrations of all these points, I will project on the screen the images of three negatives of the same object—a brightly-lit window taken on the same substance, a home-made emulsion of silver bromide. In the first the coating of emulsion was spread very thinly on an ordinary glass plate, and you see the halation is very pronounced; in the next the plate coated with film of the same thickness is backed, and you see that the halation, although still present, is much less than before; whilst in the third, in which the layer of sensitive material is  $\frac{1}{80}$ th inch thick, halation is completely absent.

If a substance reflects light at all every ray falling upon it must obey the ordinary law, but it is easily seen that a series of parallel rays reflected from a surface will remain parallel after reflexion only on condition that the surface is perfectly flat. For if the

surface is not flat rays A B C parallel at incidence will take after reflexion directions A<sup>1</sup> B<sup>1</sup> C<sup>1</sup> at all angles to each other (fig. 17).

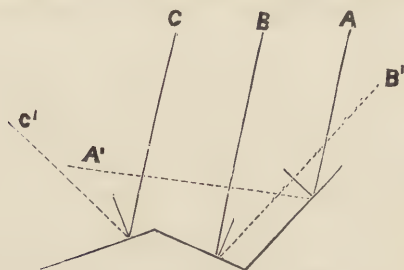


FIG. 17.—IRREGULAR REFLEXION OF LIGHT.

Now the diagram is an exaggerated representation of all ordinary surfaces, and we express the result by saying that such surfaces scatter the light falling upon them in all directions. This scattered light is both disadvantageous and advantageous in practical photography.

Let us suppose that we are using in the ordinary way a camera the inside of which has not been blackened. Now every particle of ether in the cone of rays falling upon the sensitive plate is, as we have learnt, itself capable of starting waves in all directions. Clearly some of these secondary waves will reach the sides of the camera, and being reflected therefrom will impinge upon the sensitive surface, and so tend to fog it. It is, in fact, to absorb these irregularly reflected rays that not only the interior of the camera but the inside of the lens mount, and the stop apertures, are made dead black, so as to absorb the rays and not reflect them.

Another source of trouble arises from the particles of dust floating about inside the camera and between the lens and the plate. Each one of these being capable of reflecting light acts like a solid luminous body and so produces fog.

To reduce fog arising from this cause to a minimum, and at the same time to reduce the slight reflexions from the sides of the camera (for the best dead black yet invented still reflects *some* light), many workers employ a series of screens, with gradually decreasing openings inside the camera between the lens and the plate. Under these circumstances the effect of light reflected from the sides is completely eliminated, and the quantity of light reflecting dust capable of affecting the plate is reduced to the smallest possible amount.

So far as reflexion from the sides is concerned this would be at a minimum in a large camera used for a small plate, but since the

quantity of dust present would also increase the gain in freedom from fog from one cause would evidently be a loss from the other. If, however, a series of screens were placed, as described, in a large camera, then the very best possible conditions for good work would be attained. If, instead of using a lens in a camera the back of which was larger than the plate the lens was intended to cover, a lens covering a large plate was used in a small camera, then the reflexion from the sides would be so increased (this time by a portion of the direct cone of rays) as to render good work, at least without screens, almost an impossibility.

This scattering of light, although a great evil in certain cases, is a positive blessing in others, for it enables us to photograph objects which could not be photographed if they reflected light regularly. If, for instance, a pure red surface reflected red light regularly, it would be impossible to cause its image to impress itself on the sensitive plate, but since, in addition, it scatters white light owing to its surface not being a true plane, it is possible to obtain a developable image of it. The quantity of scattered light varies inversely as the reflecting power of the substance, and a knowledge of this fact enables highly reflecting surfaces, such as a brightly polished metallic teapot, to be photographed in such a way that the resulting prints will be free from unpleasant reflexions. Causing the beam of light from the slit in my lantern to impinge upon the convex mirror in front of it, you all see the mirror, and certain of you see in addition an image of the slit reflected in it.

If a photograph of the mirror were taken from the point of view at which no image of the slit appears, the resulting negative would be free from the dark patch due to the reflected image of the slit, but it might not be possible to so alter the position of the camera as to bring about this result.

By rubbing over the mirror, however, this rag smeared with whiting and water I reduce the regular reflexion to such a small amount that no image of the slit is seen, and it follows, therefore, that the camera would now give in any position a negative quite free from the dark patch.

In this way when photographing plate, jewellery, machinery, or other highly reflecting bodies all difficulty as to where the camera should be placed is avoided if the reflecting power of these surfaces be sufficiently reduced in the manner indicated.

#### SUMMARY.

The line traced out by a solid particle impinging on a hard surface at any angle makes, with the perpendicular to the surface at the point where the particle meets it, a certain angle, viz., the *angle of incidence*, and the particle glances off, so that its new line of motion makes a similar *angle of reflexion*.

What is true of a solid particle is equally true of a wave. As a result of this the images formed in plane mirrors are *laterally*

*inverted*, hence a mirror at an angle of  $45^\circ$  in front of a lens enables the latter to produce a *reversed negative*.

The same result can be obtained by using a *right angle prism*, by turning the film from the lens, or by employing a support so thin that it can be printed from the back.

*Halation* is due to the passage of some light through the film, and the reflexion of this light from the back of the film, or the back of the support.

Increased thickness of support means increased halation, because as this thickness increases the distance also increases between the points where the incident and reflected rays meet the front surface of the glass.

Increased thickness of film means diminished halation, because in this case increased thickness means increased absorption.

By blackening (or reddening) the back of the support, halation is reduced, the waves reaching the back being now absorbed.

By blackening (or reddening) the front of the support, or the film itself, halation is still further reduced, all waves being now absorbed.

*Irregular reflexion* means scattered light. If the sides of the camera, or the dust inside, scatter light, the plate will be fogged. Blackening the sides of camera, lens mount, stop, etc., prevents this.

The freer from dust the inside is kept the less the chance of fog.

Light scattered by the bodies being photographed is beneficial, as it reduces violent contrast. The amount of scattered light is increased by dulling the surface, which should always be done with machinery, &c., or, generally speaking, with highly reflecting bodies, in order to avoid unpleasant reflexions.

## LECTURE VII.

REFRACTION AND ITS LAWS—MEASUREMENT OF ANGLES BY SINES—  
INDEX OF REFRACTION—CRITICAL ANGLE—PROOF OF THE CORRECT-  
NESS OF THE WAVE THEORY—CONNECTION BETWEEN REFRACTION  
AND REFLEXION—WHY PRINTING FRAMES ARE PLACED SQUARE  
AND LENSES CEMENTED TOGETHER WHENEVER POSSIBLE—THE  
BUNSEN OR GREASE SPOT PHOTOMETER AND ITS APPLICATIONS.

**I**N a homogeneous medium a ray of light is propagated in straight lines, but if the medium is heterogeneous then the ray is bent, such bending being called refraction.

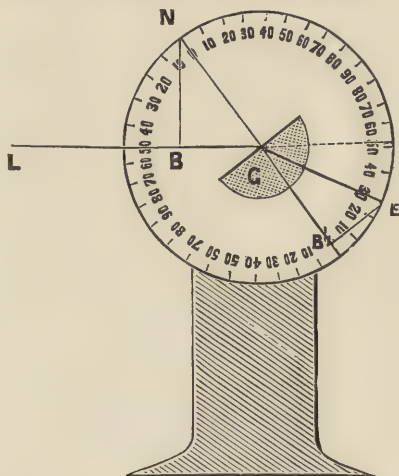


FIG. 18.—APPARATUS FOR ILLUSTRATING THE LAWS OF REFRACTION.

To illustrate this I have (fig. 18) a hemi-cylinder of polished crown glass *G* attached to a graduated cardboard circle, the whole being mounted so as to revolve on a horizontal axis. The diameter at right angles to the hemi-cylinder produced passing through the zero of the scale, the angle included between this line and a ray incident upon the plane face of the hemi-cylinder gives us in all positions the angle of incidence.



Causing now a beam of light to impinge upon the plane face so as to make an angle of incidence  $L G N$  of  $50^\circ$ , you see that the ray is bent, and takes the direction  $G E$  such that the angle  $B^1 G E$  equals  $32^\circ$ , this latter angle being termed the angle of refraction.

Rotating the graduated circle so as to cause the angle of incidence to be both greater and less than  $50^\circ$ , I measure the corresponding angle of refraction and tabulate the results thus:—

Angle of incidence.		Angle of refraction.		BN		
				BN	BE	EB
$60^\circ$	..	..	$38^\circ$	..	77	51
$50^\circ$	..	..	$32^\circ$	..	68	46
$40^\circ$	..	..	$25^\circ$	..	56	37

The lines  $BN$  are here the lengths of the perpendiculars let fall from the zero point of the scale meeting the incident rays, and the lines  $BE$  the perpendiculars let fall from the points where the refracted rays meet the edge of the scale to the zero point of the scale on the other side.

Now, a glance reveals the fact that, although no simple ratio exists between corresponding angles of incidence and refraction, the ratio between the lengths of the corresponding pairs of lines  $BN$ ,  $BE$  is always the same whatever the angles themselves may be.

The ratio  $\frac{BN}{BE}$  is, in fact, the ratio between the sines of the angles themselves, and we learn therefore that this ratio is always constant.

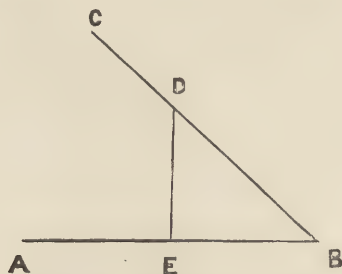


FIG. 19.—THE SINE OF AN ANGLE.

It may be well to explain precisely how the sine of an angle is arrived at.

Calling  $ABC$  (fig. 19) an angle of less than  $90^\circ$ , then if from any point  $D$  on  $CB$  a perpendicular  $DE$  is let fall on  $AB$ , we have in  $BED$  a right-angle triangle, of which  $EB$  is the base,  $ED$  the perpendicular, and  $BD$  the hypotenuse.

The ratio of the length of  $ED$  to that of  $BD$ , or, as it is usually expressed  $\frac{ED}{BD}$ , is the sine of the angle  $ABC$ , and measures its magnitude just as truly as if the number of degrees it included had been given. Now, in the previous figure, it is easily seen that the sines of a series of angles of incidence will be a series of lines drawn like  $NB$  perpendicular to  $G$  divided by what will be in every case the radius of the circle, and the same holds good with the sines of the corresponding angles of refraction.

Since the hypotenuse is the same in every case, being the radius of the circle, we get the *ratios* between the two sines in the *ratios* of the two perpendiculars, viz.,  $NB$  and  $BE$ , or lines corresponding to them.

This ratio is called the *index of refraction*, and varies with the nature of the substance, being, as we have seen, 1.5 from air to glass, but varying from this to nearly 1.8 in different varieties of the same material.

Just as with wave lengths so with refractive indices, we must use, not white light, but light of a definite degree of refrangibility, corresponding to certain of the Fraunhofer lines.

If we measure the refractive index at the  $D$  line we represent practically the bending of those rays which have the greatest luminosity, whilst if we measure it at the  $G$  line we represent the bending that ray experiences, which has the most effect upon silver iodide. For silver bromide the point to measure would be a line between  $F$  and  $G$ , and for silver chloride the  $H$  line.

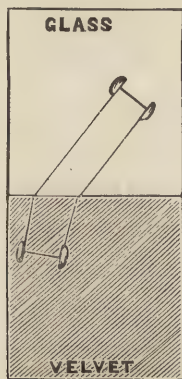


FIG. 20.—WRIGHT'S ROLLERS.

It may be interesting to trace out the reasoning adopted to explain the bending of an ether wave in passing from one medium to another.

I have here a glass plate, on one half of which is glued a piece of thick velvet plush. Causing these two small wheels connected by an axle (fig. 20) to roll over the glass so as to meet the velvet at an angle, we see that on the velvet the axle tilts round, the direction of motion on the velvet being different to the direction on the glass.

Now it is very easily seen that in the case in point this tilting is due to a retardation of the wheel which first reaches the velvet, for on again starting the wheels so that the line joining their axis is parallel to the velvet no swinging round now takes place, because both wheels meet the velvet at the same time.

If our senses were directly incapable of appreciating the fact that the wheels move more slowly on velvet than on glass, but that we could, nevertheless, satisfy ourselves that bending did occur under certain circumstances when the wheels passed from glass to velvet, we should very reasonably conclude that this bending was the effect of retardation and of nothing else.

The wheels are, in fact, types of ether waves, whose direction we call a ray of light, the glass surface is a type of the air through which that ray passes, and the velvet a type of the water or glass in which it is refracted.

Now, in the case of our wheels, the bending is the result of retardation, and the greater the retardation the greater the bending.

If light were the result of the transfer of matter from place to place, just as a bullet travels from a gun to the target, the gun being here the type of a light-producing body, and the target a type of the eye, it follows that the above law should hold good with light, viz., that its velocity should be *greatest* in that medium in which it is *most* bent, *i.e.*, in which it makes the least angle with the perpendicular.

According to this view the velocity should be greater in glass than in air, but a direct experiment proves the opposite, and we conclude, therefore, that light cannot be due to the direct transfer of *matter* from the source to the eye.

It is frequently necessary in problems in practical optics to draw the direction of a refracted ray through a substance, being given the refractive index of the substance and the direction of the ray incident upon it. Let, for instance (fig. 21), the substance in question be a plate of glass  $AB$  of a refractive index of 1.5, and let  $CD$  represent the incident ray, then, to get the direction of the refracted ray, we draw  $DF$  perpendicular to  $BD$ , and produce it, and, taking any point  $M$  on  $DF$ , we draw  $MN$ , cutting  $DC$  in  $N$ . Now, dividing  $MN$  into three parts, we join  $D$  and  $1.0$ , which, produced to  $D M$ , gives the direction of the refracted ray.

Just as refraction takes place from air to glass, so will refraction take place from glass to air, but the refracted ray will now be bent *from* the perpendicular. In fig. 21, for instance, a ray,  $M^1D$ , in glass would be refracted in air in the direction  $DC$ , and, since the

angle  $F D 1.0$  is always smaller than  $M^1 D O$ , we can now find a value for the former such that the ray does not emerge at all, but continues parallel to the surface of the glass, and if this angle is

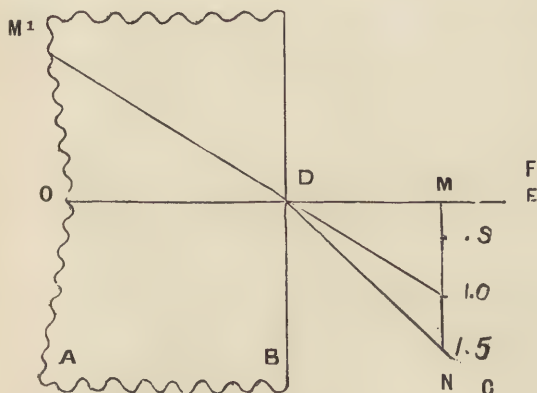


FIG. 21.—PATH OF A RAY FROM AIR TO GLASS.

exceeded, the ray becomes totally reflected as from a mirror from the surface of the glass.

Turning round my graduated circle until the hemicylinder of glass is in the position shown in fig. 22, you see that the incident ray  $L S$  no longer emerges at all, but is totally reflected from the plane face of the glass and takes the direction  $S C$ .

The angle at which a ray, passing from one medium to another, will not emerge but continue parallel to the surface of the medium is called the critical angle, and since the ray in air just grazing the horizontal surface of the medium is a right angle, the sine of which is unity, we see that the sine of the critical angle must be the reciprocal of the index of refraction. Taking, for instance, glass of a refractive index of  $1.5$ , then the sine of its critical angle will be  $\frac{1}{1.5} = .66$  and as a sine of this value corresponds to an angle of  $40^\circ$ , this is consequently the critical angle for glass of that particular refractive index.

It is easy to see that, although a portion of a ray of light incident upon, say, a glass surface is refracted, some of it must also be reflected, and I will now prove that as the angle of incidence increases the amount of light reflected increases, and the amount refracted decreases.

Causing a ray incident on the surface of the apparatus (fig. 22) to make a small angle with the perpendicular, I diminish my oxygen supply until the refracted ray is barely visible, and now, rotating

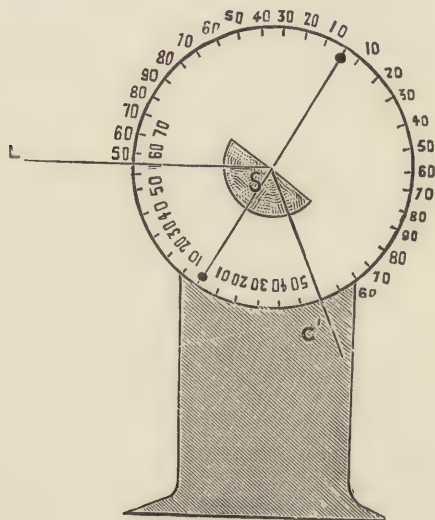


FIG. 22.—THE CRITICAL ANGLE.

the graduated circle so as to increase the angle of incidence, you see that we very soon reach a point at which the path of the refracted ray in the glass can no longer be traced.

The greater part of the light is, in fact, now being reflected off from the surface of the glass, instead of passing through it.

Now, since the amount of light reflected from the surface of a material of any thickness varies inversely as the amount refracted through and available for use at the bottom of it, we see that to get the full value of the light in printing, etc., our frames must be at right angles, or nearly so, to the direction of the light, every other angle increasing the amount of light reflected, and consequently diminishing the amount available for altering the colour, &c., of the sensitive compound.

The same thing will of course be true with a lens, for only those rays which are perpendicular to the tangent to the curve, or as we



say normal to the surface, can exert a maximum effect, the rays taking any other direction being considerably reduced in intensity.

Placing this piece of glass so that the parallel rays from my lantern fall upon it at an angle of about  $60^\circ$ , a great deal of the light is reflected, and comparatively little gets through. If I now place another plate of glass in front of the first you notice a considerable diminution in the intensity of the light, that getting through the first plate being now reflected off from the surface of the second. The more reflecting surfaces we have, therefore, the greater the loss of light, hence the more reflecting surfaces a combination of lenses possesses the less light will pass through.

Placing six plates one in front of the other, so as to make an angle of  $60^\circ$  with the axis of my lantern lens, you perceive that no light at all gets through, the successive reflexions completely extinguishing it.

If, however, I place the six plates in a glass trough containing water, and cause the whole to make the same angle with the lens, the light now passes through, the reason being that the glass plates are separated from each other by a material having a higher refractive index than that of air, and, consequently, one which differs from that of glass to a lesser degree than that of air does. It is for this reason that, whenever it becomes necessary to use two lenses of the same radius of curvature in contact with each other, we always connect the two adjoining surfaces with a layer of Canada balsam, and so reduce the loss of light to a minimum.

I can illustrate the same point in another way. Placing a piece of blotting-paper in front of the cone of rays coming from his gas flame, you see that it very considerably enfeebles the light owing

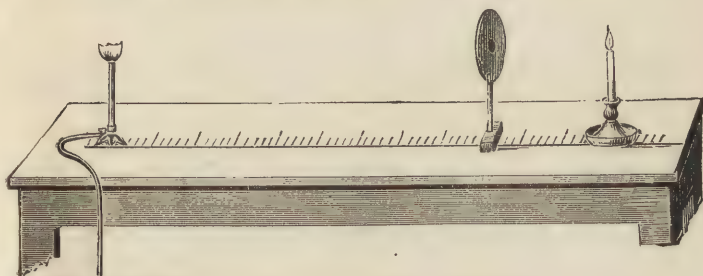


FIG. 23. — THE GREASE SPOT PHOTOMETER.

to the fact that paper is not homogeneous, but consists of a number of minute particles of cotton, linen, &c., separated from each other by layers of air, the refractive index of these particles differing from that of the air which separates them (fig. 23).

If, now, I make a dot on the centre of the paper with a little oil, you notice that the oiled spot appears brighter than the rest of the paper, more light coming through. The reason is that the oil has an index of refraction approximating more closely to that of the linen, &c., than that of air, and in consequence the reflexion is diminished, and the refraction correspondingly increased.

Clearly if this be the case, on turning the paper round so as to view it by reflected light, the oiled spot should be darker than the rest of the paper owing to reflexion at that spot being at a minimum, and on making the experiment we actually find that such is the case.

If, now, I take a candle and place the paper in front of it, *i.e.*, between the eye and the candle, the grease spot appears lighter than the surrounding portions of the paper, but if I place the paper behind the grease spot appears darker, and taking two similar candles and placing one in front and the other behind, you see that the grease spot disappears, the same fact holding good at any reasonable distance of one candle behind the paper, provided the other candle is at an equal distance in front of it.

— We have, in fact, in the piece of paper a Bunsen or grease spot photometer, by means of which we can compare the relative intensities of two sources of light.

Removing my lantern tray, I place it and the incandescent lime at 20 feet from the paper, and alter the distance between the candle and the latter until the grease spot disappears. Now measuring the latter distance I find it to be 16 inches, from which I calculate the intensity of the limelight as being equal to  $\frac{240^2}{16^2} = 225$  candles.

#### SUMMARY.

The *sine of the angle of incidence* of a ray of light in air bears to the *sine of the angle of refraction* of the ray when passing through another medium a constant ratio.

This ratio is the *index of refraction* of the substance in question referred to air as unity.

*Indices of refraction* measured at Fraunhöfer's *D* line give the degree of bending which the rays of greatest visual intensity undergo.

Since the rays exerting greatest action upon any substance depend upon its nature, we cannot, properly speaking, give the degree of bending which the rays of greatest chemical activity undergo unless we know the substance upon which they are supposed to act.

The *velocity of light in glass* has been experimentally found to be less than its velocity in air.

Light cannot, therefore, be due to the transmission of matter from one spot to another.

Light incident upon any substance is partly refracted and partly reflected, the *greater the refraction the less the reflexion*, and *vice versâ*.

To avoid *loss of light by reflexion* we place our printing frames square to the light and cement our lenses together with Canada balsam.

The *greater the number of reflecting surfaces* a lens possesses the *slower* it will be. A doublet worked full aperture is *slower* than a single lens of the same focus and aperture.

The grease spot photometer depends on the fact that a *grease spot* on paper viewed by *reflected light* seems darker than the paper, whilst by *transmitted light* it seems brighter. If it cannot be seen at all, then the amount of light transmitted is the same as that reflected.

## LECTURE VIII.

REFRACTION OF LIGHT THROUGH MEDIA WITH PARALLEL FACES—  
PRECAUTIONS TO BE OBSERVED IN ORTHOCHROMATIC WORK—  
REFRACTION THROUGH A PRISM—DEVIATION—ANGLE OF MINIMUM  
DEVIATION—DISPERSION—ACHROMATIC PRISMS—DIRECT VISION  
PRISMS—USE OF PRISMS IN THE PRODUCTION OF REVERSED  
NEGATIVES.

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WE considered in the last lecture only the bending which a ray of light experiences in passing from air to water or glass, but this is evidently only a part of the question, for in every practical application of the laws of refraction the ray not only passes from air to the material, but emerges from the material to air.

We must, therefore, now consider the bending which a ray of light experiences on passing from, say, glass to air.

Taking, as typical, a plate with parallel sides made of glass of refractive index 1.5, we can, in the manner already indicated, draw the course of the incident and refracted ray, and a similar method

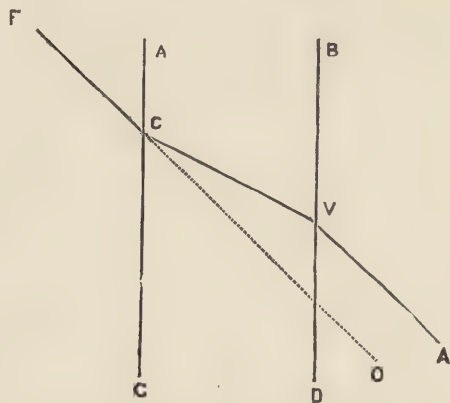


FIG. 24<sup>1</sup>—PASSAGE OF RAY OF LIGHT THROUGH GLASS PLATE WITH  
PARALLEL SIDES.

of reasoning to that adopted in tracing the direction of the refracted ray enables us to follow the track of that ray upon emergence.

Representing in fig. 24 the sides of the glass plate by  $ACBD$ , then if  $AV$  is the incident ray, its direction after refraction will be  $VC$ , and it will on emergence take the direction  $CF$ .

It is easy to see that under the given conditions, *i.e.*, if the refracting substance is made with parallel sides, the emergent ray  $CF$  must be parallel to, although not in the same straight line as the incident ray  $AV$ .

It follows from the foregoing that any object at  $A$  viewed by the eye at  $F$  will be seen in the direction  $FO$ .

If, then, we interpose a plate of glass between the lens and sensitive plate, the image of the margins of the object photographed being at  $A$  will be displaced on the sensitive plate towards  $O$ , and this displacement must, of course, result both in distortion and in loss of sharpness.

If the glass plate is exceedingly thin, the line  $CF$  is sensibly in the same direction as  $AB$ , and the nearer the plate is to the lens the less displacement will occur.

Hence, if we must use such a plate in orthochromatic work, we should take care that it is as thin as possible, and that it is placed as close to the lens as possible if the latter is a single one, or in the diaphragm slit if the lens is of the doublet form, in both of which positions it will practically coincide with the nodal point of emission of the lens.

I can illustrate the effect by projecting upon the screen the image of a square, which, with my non-distorting lens, remains a square, but if I now interpose between the lens and the screen this piece of thick plate glass, you see that not only has a considerable loss of definition occurred, but the sides of the square are now curved inwards or distorted.

If the edges of the refracting substance are not parallel, but

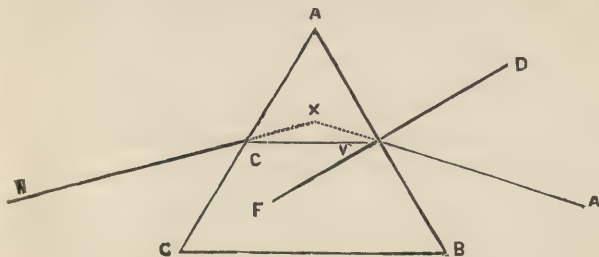


FIG. 25.—PASSAGE OF A RAY OF LIGHT THROUGH A PRISM.



inclined to each other, we get a different result, for in this case the bending of the refracted ray in the material due to refraction will be intensified by the fact that the emergent ray leaves a surface which is inclined to the first one.

Taking as type the section of a glass prism (fig. 25) a ray A B incident upon the face A B will take, after refraction, a direction B C such that  $\frac{\sin A B D}{\sin C B F} = \frac{3}{2}$ , to arrive at which direction make use of exactly the same method of construction as before.

The angle included between the original direction of the ray and its direction upon emergence is called the angle of deviation, and C A B is the refracting angle of the prism itself.

Let us now consider what would occur if the apex A of the prism was gradually tilted round to the right, the whole rotating upon A as an axis. Clearly by swinging round the prism in this manner up to a certain point we should cause the angle of deviation to decrease, but beyond that point the angle of deviation would increase.

Projecting on the screen the image of a slit, behind which is a plate of pure red glass, I place this prism in the track of the ray, when you see that the image is deflected to one side. Now, gradually tilting the prism, the image makes a smaller and smaller angle with its original position, but on tilting the prism still more the angle again increases.

The minimum angle made is here the angle of minimum deviation, and this point is obviously reached when the path of the ray in the prism is parallel to its base.

Measuring now this angle of minimum deviation by the chord of the arc, which it subtends, I find it to be 12 inches.

Replacing my first prism with one having a greater angle I again find the position of minimum deviation, and now, measuring the chord of the arc, I find this to be 13 inches, so that as the angle of the prism increases so does the angle of minimum deviation.

Taking now, instead of the flint glass prism just used, one of crown of the same angle, and again finding the angle of minimum deviation, you see that the chord is less than 13 inches, hence the higher the refractive index of the substance the greater the angle of minimum deviation.

Knowing, in fact, the angle A of a prism of any material and the angle A of minimum deviation, the refractive index R of the material can be at once calculated from the formula  $R = \frac{\sin \frac{1}{2}(A+A)}{\sin \frac{1}{2}A}$  and this gives a ready way of calculating the refractive indices of transparent solids or of liquids enclosed in prismatic glass cells.

Replacing my ruby glass by a piece which transmits pure blue light, you see that the angle of minimum deviation has increased.

It is, therefore, necessary in determining refractive indices to do so with light of a definite degree of refrangibility, an easy method of arriving at this being afforded by the Fraunhofer lines.

Why was the angle of deviation at a minimum using red light, and at a maximum when violet was employed? Clearly because the frequency of the ether waves resulting in violet light is greater than the frequency of those resulting in red light, and it is precisely because rays of different frequencies are bent to different degrees that a prism enables us to decompose white light into what we call the prismatic spectrum.

Taking now two prisms of the same angle and of the same material, I turn them opposite ways, so that the base of one is against the edge of the other, and, putting the two in the track of a beam of white light, you see that we have neither deviation nor dispersion. One prism has, in fact, undone the work of the other, the rays separated from each other by the first prism being caused to overlap by the second. Clearly, however, the result would occur only on condition that the prisms were in absolute contact, for if they were not the overlapping of the rays necessary to produce their perfect recombination could not occur.

Now it is evident that by altering the angles and the material of the prisms we can produce at will either deviation without dispersion, or dispersion without deviation.

Let us first consider how we can construct an achromatic prism, as one which deviates a ray without dispersing it is called.

We must begin with the self-evident statement, that the ratio between the dispersion of two materials is given by the lengths of the spectra they respectively yield, when made into prisms having the same angles.

Thus, flint is said to be more dispersive than crown glass, because a prism of flint will yield a longer spectrum than one of crown.

I have here two such prisms, and placing them one over the other so as to cause the two spectra to fall one above the other you see that the spectrum yielded by the flint is longer and more deviated than that yielded by the crown.

You will, however, notice that although the flint prism deviates the spectrum as a whole very much more than the crown, yet the dispersion it yields, *i.e.*, the length of the spectrum it gives, is not increased in the proportion which the increased deviation might lead us to suppose.

Now, if I take these prisms and place them edge to base, the deviation is less than before, being now the difference between the two deviations, and dispersion is all but absent.

It will, however, be readily understood that I could, by *very slightly* reducing the angle of the flint prism, reduce its dispersion to exactly the same amount as the crown, without, at the same time, reducing its deviation in the same proportion.

Here I have two such (fig. 26) complementary prisms, as they are called, and placing them as before one over the other, you notice that the dispersions are equal, although the deviation of the flint is greater than the crown, and now placing them base to edge



FIG. 26.—DEVIATION WITHOUT DISPERSION (ACHROMATIC PRISM).

we get a combination which deviates a beam of white light, but does not disperse it in the least.

We have got, in fact, in the pair of prisms an achromatic combination.

In photography, however, it is not so much a question of getting no dispersion as of equally dispersing those rays which are brightest and those which act most energetically upon the usual sensitive compounds.

Now, the portion of the solar spectrum giving most light lies practically at the D line, and leaving silver chloride out of count, that portion which acts most energetically upon silver bromide and iodide lies practically at the F line. Hence, for photographic purposes, we endeavour to achromatise, so that the most visible rays at the D line will be dispersed to the same degree as the most active rays at the F line, and so ensure that our visual focus shall coincide with our actinic one.

We learn from this that a telescope or microscope lens perfectly corrected for colour would not be suitable for photographic purposes, and, *vice versâ*, that the occurrence of a slight amount of dispersion in a photographic lens may be a proof of its goodness rather than of the reverse.

Having learnt how deviation may be secured without dispersion, we will next consider how the converse problem is dealt with, viz., the production of dispersion without deviation.

In examining a spectrum, it is evidently an inconvenience for the emergent ray to have to be viewed in a direction making an angle with the incident one, and this is particularly the case when we are examining, not a comparatively steady source of light like the sun, but a source of light which is constantly varying in position, such as, for instance, the light emitted by a meteor or comet.

In such a case as the last the convenience of being able to point the prism at the source is too obvious to need comment, and this means, of course, if a spectrum is looked for, dispersion without deviation.

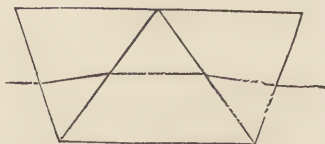


FIG. 27.—DISPERSION WITHOUT DEVIATION (DIRECT VISION PRISM).

Now a prism of flint of any angle cannot be matched, so far as deviation is concerned, by a prism of crown of some other angle, but by taking *two* prisms of crown it is quite possible to adjust their angles that the sum of the deviations they give equals that given by a single flint prism. Evidently, however, since the dispersion of the flint will be greater than that of the two crowns, the combination will disperse and not deviate. Such a combination, called a direct vision prism, is shown in fig. 27, and is useful for many purposes, although, of course, owing to the thickness of the materials used, the spectrum it yields is much less bright than that yielded by a single prism.

Evidently the critical angle of the material used for a prism will determine the maximum angle the prism itself can possess if a ray is to emerge at all, and it can be easily shown that this angle must be less than twice the critical angle of the substance in question.

It is for this reason that substances of high refractive indices are preferred for prisms, since their employment means a comparatively small angle of deviation with relatively large dispersion.

Prisms of more than twice the critical angle of the substance of which they are made are, although useless for producing spectra, exceedingly useful as reflectors.

In the case of the right-angled prism of crown glass, shown in fig. 28, a ray *A V* falling perpendicularly on one face proceeds in a straight line, and meeting the base makes, with the perpendicular, an angle of  $45^\circ$  greater than  $40^\circ$ , the critical angle of crown glass.

In consequence of this the ray is totally reflected, and emerges without deviation in the direction *V C*. Since, of course, the prism acts as a mirror a lens placed at *C* would project upon the



ground glass a laterally inverted image of an object at A, and so yield a "reversed" negative.

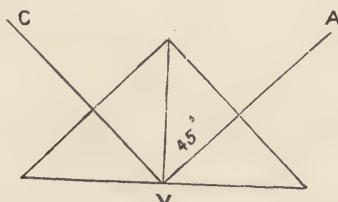


FIG. 28.—TOTAL REFLEXION (RIGHT-ANGLED PRISM).

Right-angle prisms are frequently used in this way instead of mirrors, and possess over the latter the advantage of not being readily tarnished.

#### SUMMARY.

A ray of light passing through a medium with parallel faces—*e.g.*, a glass plate, emerges parallel to its original direction—a square viewed through such a plate is distorted into a pin-cushion. Hence, if a lens gives barrel-shaped distortion we can remedy this by placing a glass plate between lens and plate. But the use of such a plate means a loss in definition, unless the plate is very thin and very close to the lens, best at the nodal point of emission of the latter.

A ray of light passing through a prism is bent *from* the refracting edge of the prism. This bending or *deviation* is at a *minimum* when the angle the incident ray makes with the incident edge equals that which the refracted ray makes with the refracting edge.

*The greater the angle of the prism itself, the material remaining the same, the greater the angle of minimum deviation.*

*The higher the refractive index of the material of which the prism is made, the greater the angle of minimum deviation.*

A knowledge of the angle of a prism, and the angle of minimum deviation of a ray of *definite refrangibility* (say Fraunhöfer's D line) passing through it, enables the *refractive index of the material* to be calculated.

Since rays of different refrangibility are *unequally* bent, a prism *disperses* white light.

Dispersion is measured either by the length of the spectrum a prism of the material yields, or by the difference in minimum deviation for any two lines.



*Dispersion not increasing or decreasing in the same ratio as deviation, a compound prism can be made giving deviation without dispersion (achromatic prism) or dispersion without deviation (direct vision prism).*

To obtain achromatism, we select two prisms of *different materials*, having such angles as to give equal dispersions, and cement them base to edge.

Achromatism (absence of colour) as applied to telescopes, &c., is not synonymous with photographic achromatism.

In photography we want not absence of colour, but equal deviation of the rays *visually brightest* (D line), and of those *most active* upon the *usual silver compounds* (F line).

A crown glass prism of  $90^\circ$  acts as a reflector, because a ray meeting it at right angles to the base suffers no deviation, and meeting the hypotenuse makes an angle of incidence of  $45^\circ$  greater than the *critical angle of crown glass* ( $40^\circ$ ), and is totally reflected from the hypotenuse, passing out at right angles to the perpendicular without deviation.

## LECTURE IX.

UNEQUAL BENDING OF RAY OF LIGHT MEETING DIFFERENT PORTIONS OF A PRISM—SIMILARITY BETWEEN PRISMS AND LENSES—TYPES OF LENSES—SPHERICAL ABERRATION AND ITS CAUSE AND CURE—CHROMATIC ABERRATION—ACHROMATISM—VARIETIES OF OPTICAL GLASS.

THE further study of the properties of prisms affords a valuable introduction to that of lenses, and we will therefore begin by investigating what occurs when a ray of monochromatic light meets a prism at varying distances from its apex.

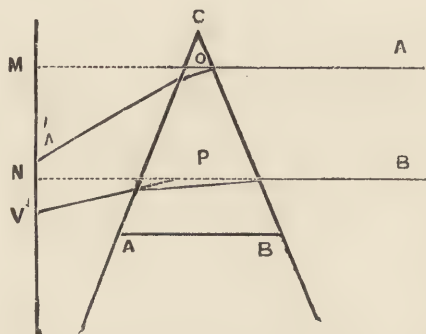


FIG. 29.—UNEQUAL DEVIATION BY APEX AND BASE OF PRISM.

Taking the prism  $ABC$ , I place it, base downwards, upon its support, and direct a parallel ray,  $AM$ , of monochromatic light from my lantern upon its top edge, when you see that the emergent ray meets the screen at  $A^1$  (fig. 29).

Now, raising the prism, I cause the ray  $BN$  to meet it nearer to its base, and we get the image formed at  $V^1$ , the angle of deviation being now smaller than before.

It follows from this that a ray meeting a prism near its apex is more bent than another ray parallel to the first meeting the prism near its base.

If, now, we take two prisms of the same material and angle, and place them, base to base, one over the other, then parallel rays of monochromatic light meeting the incident edges will be equally bent, and meet at a point behind the prisms.

But evidently, if the pair of parallel rays had taken a direction nearer the centre, then they would have been relatively less bent, and would have now met further off (fig. 30).

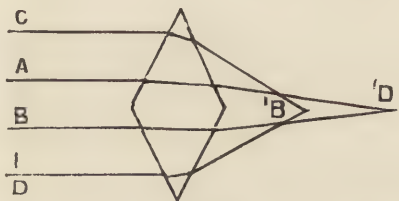


FIG. 30.—A LENS CONSIDERED AS TWO PRISMS.

To get the same degree of bending for the rays A B as for the rays C D, or, what amounts to the same thing, to get each pair of rays to converge towards and meet at the same point behind the prism, the inclination of the refracting edge to the first pair of rays would have to be the same as the inclination of the same edge to the second pair.

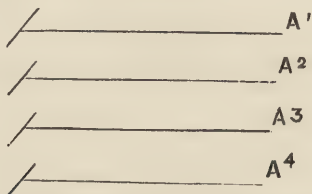


FIG. 31.—PARALLEL SURFACES GIVING UNEQUAL DEVIATIONS.

Letting  $A^1$ ,  $A^2$ ,  $A^3$ ,  $A^4$ , in fig. 31 represent four parallel rays, then to get equal refractions in the refracting material its edges should have the degrees of inclination shown—a result of course impossible in a prism of the usual construction.

Now we may look upon a curved surface as made up of an infinite number of plane surfaces whose edges are inclined to each

other, the degree of inclination at any point being measured by the angle included between lines normal and tangent respectively at the curve at that point.

In fig. 32 let  $V C D G$  represent a spherical glass surface, then lines drawn from the surface to the points  $V C$  on the curve are normals to the curve at those points, and lines at right angles to these are tangents to the curve.

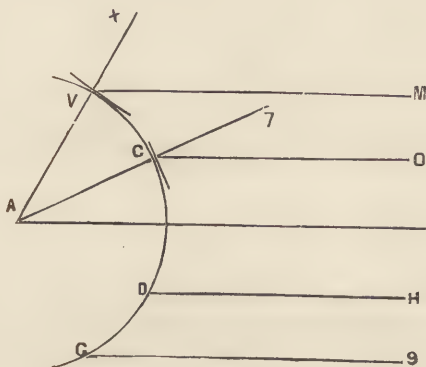


FIG. 32.—INCLINED SURFACES GIVING EQUAL DEVIATIONS.

Now so far as monochromatic light is concerned, a ray  $M V$  would be refracted to the same degree by such a curved surface as by a plane one tangent to it, and the same would hold good with any other ray.

To get an equal degree of bending for all the rays we should require not a spherical but a parabolic surface. Owing, however, to the great difficulty of grinding such a surface we content ourselves with one of the spherical form, but introduce thereby certain defects in the images given by lenses whose surfaces are spherical.

Lenses whose surfaces are portions of spheres are capable of being divided into two categories, according as they converge or diverge a ray of light passing through them.

Converging lenses correspond, in fact, to two prisms placed base to base, diverging lens to two prisms placed apex to apex.

In each category we have three types of lenses, named according to their shape.

Thus, in fig. 33, 1, 2, 3 are converging lens, 4, 5, 6 diverging lenses, 1, 4 being bi-convex and bi-concave, 2, 5 plano-convex and

plano-concave, and 3, 6 menisci, the former of which is commonly spoken of as a converging, the latter as a diverging meniscus.

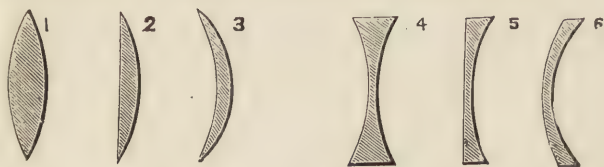


FIG. 33.—TYPES OF SIMPLE LENSES.

A glance at the diagram will show that converging lenses are thicker at the centre than at the edges, the reverse being true of diverging lenses.

Now we may look upon an object illuminated by monochromatic light as a multitude of light-reflecting points, its image formed by a lens being the result of the meeting of the rays emitted by each of these points at one and the same point behind the lens.

Confining our attention to a single point on the object, it is clear that to get a perfectly sharp image of that point the rays proceeding from it and meeting the margins of the lens must be bent to the same degree upon emergence as the rays meeting the central portions of the lens.

If this is not the case the overlapping of the two sets of rays will give the image of a circle instead of a point, the arc subtended by which will measure the sharpness of the image. If this arc subtends less than a minute, we say the image is sharp; if more than a minute, we look upon the degree of sharpness as unsatisfactory.

Now since in a single lens having spherical surfaces the marginal will always be greater than the central bending, we say the resulting want of sharpness is due to spherical aberration, or the aberration caused by the spherical form of the surfaces themselves.

But of course the object to be photographed is usually illuminated, not by monochromatic but by white light, which is more or less split up or decomposed by the lens into the rays of various refrangibilities constituting it.

It is quite true that the top of the lens refracts and disperses in one direction, and the bottom of the lens in the opposite, and since the lens is of the same material, refraction and dispersion are equal and opposite. But in order to get the two spectra to neutralise each other the rays in one must be parallel to those in the other, and this cannot of course be the case with a lens.

Projecting a disc of white light on the screen by means of this bi-convex lens you see that the edges are coloured, although the



central portions are colourless, a result which we could of course at once foresee, since the want of parallelism between the rays in the two spectra is at a minimum at the centre and at a maximum at the margin.

Now since the rays of comparatively great luminosity are those of least refrangibility, and the rays of slight luminosity those of greatest refrangibility, it follows that the latter rays will be more bent than the former, and will consequently meet at a point nearer the lens.

A lens may, therefore, bend rays of monochromatic light to an equal degree, but may, nevertheless, unequally bend the different rays co-existing in white light.

If, then, we were to cause the image of an object illuminated by white light to be formed by such a lens, the visually brightest rays, which may be looked upon as those by whose aid we focussed the image on the plane of the ground glass, would meet further off than the rays having most action on the sensitive plate, with the result that on substituting the latter for the ground-glass the visually sharp image would have for counterpart a negative wanting in sharpness, a result due to the fact that the *point* of convergence of the rays having most action on the plate was in front of the plate upon which, therefore, all points are rendered as circles of confusion.

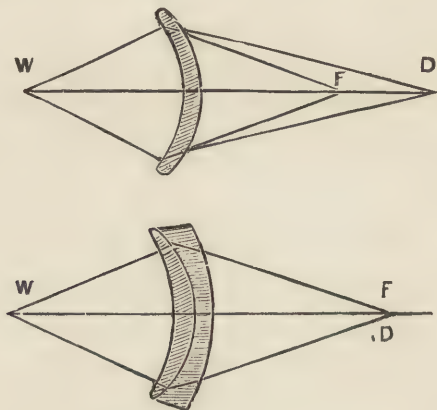


FIG. 34.—CORRECTION OF CHROMATIC ABERRATION IN A LENS.

An achromatic lens should cause the visually brightest rays at the D line, and the most active rays at, broadly speaking, the F line, to converge to one and the same point. Let us reason out

how this is effected in practice. Representing by W, in fig. 34, a point reflecting white light in front of a non-achromatic lens, then certain rays would converge at F and others at D.

By combining, however, such a lens with another of opposite form and of suitable curvature, it is easily seen that it would be possible to cause F and D to converge to the same point.

What relation should hold good between the curves and materials of the two lenses in order to arrive at this result?

We have already learnt that the ratio between the dispersions given by two kinds of glass is measured by the lengths of the spectra which two similar prisms of them would yield, or, what amounts to the same thing, by the difference between their refractive indices for the A and H lines. Practically, however, for reasons which it would be out of place to discuss, the interval C F is found to give a better result for photographic purposes, and we may, therefore, define the dispersion of a substance as the difference between its refractive indices for the C and F lines.

Since refractive indices are referred to air as unity, we get the dispersive powers of two substances by dividing their refractive indices for the D line less 1 by the difference between their refractive indices for the interval C F, or calling P the dispersive power, then D, C, F the refractive indices for the lines in

$$\text{question, then } P = \frac{D-1}{F-D}$$

In the subjoined table some of the leading varieties of glass made by Chance, of Birmingham, and by the celebrated factory at Jena, are given, together with their refractive indices for the D line, their dispersions for the interval C F, and the reciprocal of their dispersive powers as already defined.

Kinds of Glass			Refractive index for D line.	Dispersion for interval of C F.	Reciprocal of Dispersive power.
Chance.					
Hard crown	..	..	1.5179	.00860	60.2
Soft crown	..	..	1.5151	.00910	56.6
Titanic crown	..	..	1.5432	.01021	53.2
Light flint	..	..	1.5738	.01385	41.4
Dense flint	..	..	1.6202	.01709	36.2
Extra dense flint	..	..	1.6489	.01919	33.8
Double dense flint	..	..	1.7174	.02434	29.5
Jena					
Silicate crown	..	..	1.5258	.00872	60.2
Borate crown	..	..	1.5047	.00840	60.0
Silicate crown	..	..	1.5368	.01049	51.2
Borate flint	..	..	1.5736	.01129	50.8
Phosphate crown	..	..	1.5590	.00835	66.9
Borate flint	..	..	1.5503	.00996	55.2
Barium phosphate crown	..	..	1.5760	.00884	65.2
Calcium silicate crown	..	..	1.5179	.00860	60.2
Boro-silicate flint	..	..	1.5303	.01114	49.4

Causing this converging meniscus to project the image of a disc of light on the screen, you see that the edges are coloured, owing to the fact that the lens is not achromatic; but placing behind the converging meniscus this diverging meniscus, having a suitable refractive power, we get a colourless disc of light, the combination being achromatic.

What should be the ratios between the refractive powers of the two lenses in order to get this result?

Clearly they should be in the direct ratios of the reciprocals of their dispersive powers, for then the two dispersions would be corrected. Calling  $R$  and  $R_1$  the refracting powers of the two lenses, and  $D$  and  $D_1$  their dispersive powers, then we must satisfy the equation  $\frac{R}{R_1} = \frac{D_1}{D}$ . If, for instance, we made a converging

lens of Chance's hard crown, and wished to correct it with a diverging lens of the same maker's dense flint, then the refractive powers of the two lenses would have to be so chosen that the ratio between them was 60.2 to 36.2; and since the refractive power of a compound lens depends, not upon its actual shape, but upon the foci of its component lenses, we see that we can make an achromatic compound lens of any shape we please.

I now place in front of my lantern condenser a plate of finely-ground glass, on which parallel lines have been ruled, so as to form a series of squares, and illuminating this by monochromatic light, I cause the non-achromatic converging meniscus to project an image of the lines on the screen. The image is, as you see, wanting in sharpness—a result due to the spherical aberration of the lens. Now, placing a small stop in front of the lens, we thereby cause the sharpness to considerably increase; and removing the lens, I place behind it the diverging meniscus, which also corrected its chromatic aberration, and you now see that it projects an image much sharper than before. We can, therefore, correct a lens for spherical aberration either by stopping it down, or by using with it a correcting lens of a suitable degree of curvature.

As regards the action of the stop, it is easy to see, by referring to fig. 35, that the smaller the aperture of the lens the smaller will be the difference in the degrees of bending which the marginal and axial rays undergo, and as regards the action of the second lens, we can understand that it acts as shown owing to its curves being so chosen as to cause the bending of the marginal rays to be practically equal to that of the axial ones.

Thus in fig. 35  $D$  would converge after having passed through the margins at  $D^1$  and after again nearer the axis at  $D^2$ , but in fig. 34 the greater marginal bending given to the ray by one lens is compensated by the lesser marginal bending given to it by the other, with the result that all rays from  $D$  passing marginally or axially meet at  $D^1 D^2$ .

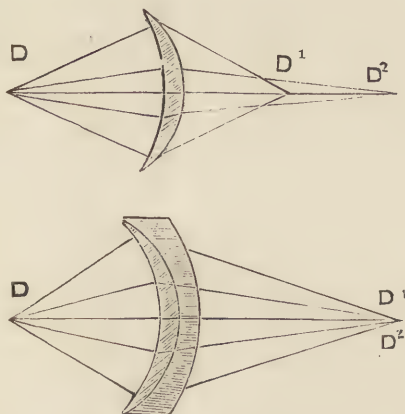


FIG 35.—CORRECTION OF SPHERICAL ABERRATION IN A LENS.

The correction for spherical aberration depends in fact, not upon the actual foci of the pair of lenses used, but upon their relative shapes, and it can be shown that with two suitable samples of glass we can make lenses of two shapes only in which chromatic and spherical aberration will be both corrected, although we might construct a number of lenses of different shapes free from either of these aberrations.

## SUMMARY.

Rays of monochromatic light making *different angles* with the incident edge of a prism are *unequally refracted*.

Two prisms placed base to base would cause two rays making *equal angles* with their two incident edges to meet at the *same point* on the other side of the prisms, the rays being caused to *converge*.

A *convergent lens* may be likened to two *prisms* placed *base to base*.

Lenses are made with *spherical* surfaces, not because this is the *best form*, but for *convenience* in grinding such surfaces.

A portion of a *circle* will then represent one side of a *lens*.

The *normal* to the curve at any point on a *circle* is the line joining that *point* and the *centre*, the *tangent* a line at *right angles* to the *normal*.

A *divergent lens* may be likened to two *prisms* placed *apex to apex*.

Lenses, like prisms, *disperse* as well as *refract*, hence the *point of greatest visual sharpness* does not coincide with that of *greatest photographic activity*.

An *achromatic* lens is one in which *both* points coincide, and consists of a *pair* of suitably chosen *lenses*.

Rays making *different angles* with the tangents to the curve at different points of a lens are *unequally refracted*, hence loss of sharpness due to *spherical aberration*.

*Spherical aberration* may be corrected by *limiting* the available aperture, by using a *suitably chosen pair of lenses*, or by both means combined.



## LECTURE X.

PRINCIPAL AND SECONDARY AXES OF A LENS—NODAL POINTS AND THEIR DETERMINATION—RELATION BETWEEN CONJUGATE FOCI—DETERMINATION OF PRINCIPAL FOCUS—ANGLE OF FIELD OF VISIBILITY AND OF DEFINITION—VARIATION OF THIS LATTER ANGLE CAUSED BY STOPS—CONNECTION BETWEEN LONGEST DIAMETER OF PLATE COVERED—PRINCIPAL FOCAL LENGTH AND ANGLE OF FIELD OF DEFINITION.

THE principal axis of a lens is the line joining the centres of its two surfaces, and through two points on this line rays of every degree of incidence must pass.

The existence of those two points, called respectively the nodes of admission and emission, I can prove in the following way.

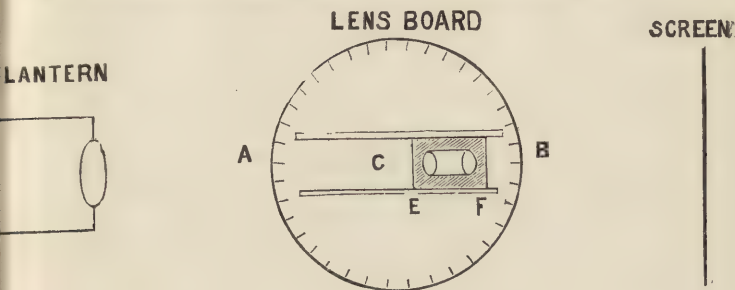


FIG. 36.—LENS BOARD FOR USE IN TESTING.

Over a circle of wood (fig. 36) A B pivoted on an axis at C is a movable piece E F capable of motion from A to B on which a lens can be placed. Under these circumstances it will be readily understood that the motion of the sliding piece E F will bring any point on the lens over the axis of rotation at C. Placing my single landscape lens on E F I cause it to project on the screen the image of the slit in front of the lantern condenser, and after having focussed I rotate the support A B, and consequently the axis of the lens, through an angle of  $10^\circ$ , when you see that the image on the screen also moves.

Now, pushing forward the support E F, and repeating the experiment, I find that the deflection of the image is smaller than before, and by a succession of trials I soon find a position for the lens in which rotating the board no longer causes the image to rotate.

When this position is reached the axis of rotation coincides with one of the nodal points, for by definition through these points rays of every incidence must pass.

As the formation of the image is the result of rays emitted from the lens we call the point we have arrived at the node of emission, and direct measurement shows us that it is, in the particular lens we are using,  $\frac{1}{2}$  in. behind the centre of the convex surface of the lens.

Now, turning the lens completely round so that the surface usually facing the ground-glass faces the object, I find, in a similar way, the position of the other node, and again measuring its distance we find that it is  $\frac{1}{2}$ th inch in front of the convex surface. Both nodes, therefore, coincide in a lens of this type, and are outside the lens, but it by no means follows that they coincide in all lenses, and occupy the same position with respect to the lens itself. Substituting for my single lens a symmetrical doublet I repeat the experiment, and find that the nodal point of emission is now between the combinations and at about  $\frac{1}{4}$ th inch behind the stop, whilst the node of admission is also between the lenses, but at about  $\frac{1}{4}$ th inch in front of the stop.

Again, repeating the experiment with a portrait lens of the Petzval type, I find that the nodes are between the lenses, but are this time crossed, i.e., the node of emission is about  $\frac{1}{3}$ rd inch in front of the stop, and that of admission  $\frac{1}{4}$ th inch behind it.

It is extremely important to know the actual positions of these nodal points, for reasons which we shall learn in a moment.

I have here a deal board eight feet long, the edge of which is graduated into inches and tenths, and at one end of it is a large gas flame illuminating a square aperture two inches across, cut in a piece of blackened tin-plate, the light being equalised by a piece of ground-glass placed behind the aperture.

Capable of sliding to and fro on the board is a sheet of ground-glass, on which are ruled a series of squares, whose sides gradually increase in length from  $\frac{1}{2}$  in. to 8 in., and a separate support to carry a lens also slides along the board.

Taking now my single lens, I place it on its support, so that its nodal point of emission is exactly over the mark on the side of the board in the same line as the divisions on the scale, and moving the screen and lens to and fro I find, by trial, a position at which a sharp image of the 2 in. square falls on the  $\frac{1}{2}$  in. square ruled on the ground glass.

Repeating the process, so as to get a series of images of gradually

increasing size, I note the distances at which they were formed, and tabulate the result thus:—

Lineal Dimensions of Object.	Lineal Dimensions of Image.	Distance of Object ( $f$ ) from Node of Emission.	Distance of Image ( $f_1$ ) from Node of Admission.	$\frac{ff}{f+f}$
2	$\frac{1}{2}$	24.8	6.2	4.9
2	1	15.0	7.5	5.0
2	2	10.0	10.0	5.0
2	4	7.5	30.0	5.0
2	6	6.6	19.8	4.9
2	8	6.2	24.8	4.9

The table at once shows that the linear dimension of the object is to that of the image as the distance of the object from the node of admission is to that of the image from the node of emission.

Any pair of corresponding distances are called conjugate foci, being, of course, mutually related, the object of small size at one focus giving an image of larger sizes at another, or *vice versa*. The fifth column shows that in every case the product of the two distances divided by their sum gives a constant quantity.

Now, if we went on increasing the greater distance more and more, the shorter distance would become smaller and smaller, until finally the greater distance  $f$  would become so great as to be out of all proportion greater than the lesser distance  $f_1$ , and when this would occur evidently  $\frac{ff_1}{f+f_1}$  would be practically the same as  $\frac{ff_1}{f_1}$  and this, again, the same as  $f$  itself.

Calling, for instance, the two distances at which this result would be obtained 100,000 and 2, then  $\frac{100,000 \times 2}{100,000 + 2}$  sensibly equals  $\frac{100,000 \times 2}{100,000}$  which is, of course, 2, or the lesser distance.

Now, the lesser distance would be, in this case, the focus for objects at an infinite distance, or of those emitting or reflecting parallel and not divergent rays, and this distance denoted by  $F$  is evidently such that the relation  $F = \frac{ff_1}{f+f_1}$  always holds true.

We have, in fact, just determined the principal focus of the lens in question, but it is evident that to do so we must know the position of its nodal points.

The method adopted, although convenient, is not, however, very accurate, a better plan consisting in causing a sharp image of the sun or of a star to fall on the ground glass of the camera. On then measuring with a rule the distance between the ground glass

and the back of the lens, and deducting from or adding to, according as we deal with a single lens or a doublet, the previously determined distance between the back of the lens and the node of emission, we have at once the desired result.

Knowing, then, the principal focus of a lens, we can calculate out any pair of corresponding foci, or ascertain the distance at which the object and ground-glass must be from the nodes of admission and emission for any required degree of enlargement or reduction.

Lenses are, as you well know, sold as covering plates of such and such a size, and we must next learn what relation exists between the focal length of a lens and the size of the plate it will cover.

We must approach this question by learning what is meant by the field of visibility of a lens.

Placing my single lens on its rotating support so that its nodal point of emission coincides with the axis of rotation, I gradually swing round the axis of the lens, and you see that, although the image does not move, it nevertheless completely disappears when the lens is swung round through a certain angle.

The angle at which this occurs is evidently, under the conditions under which the experiment was made, half the solid angle included by the field of visibility.

Measuring the semi-angle, I find it to be about  $50^\circ$ , the angle itself being, therefore,  $100^\circ$ .

Now, inserting this small stop in front of the lens, I repeat the experiment, and find that the field of visibility is reduced to  $60^\circ$ , so that with a lens of this type a stop reduces the field of visibility, for reasons which fig. 37 makes quite plain.

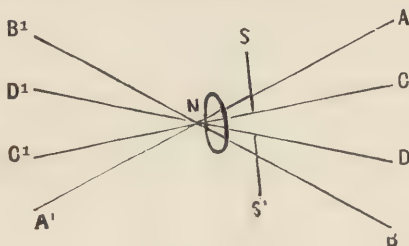


FIG. 37.—INFLUENCE OF DIAMETER OF STOP UPON FIELD OF VISIBILITY OF A LENS.

Calling N the nodal point of emission (fig. 37) of the lens, then all rays A B C D pass through it. Now if the lens is used without any stop evidently the angle A N B is greater than C N D, that



included when the stop  $S S^1$  is placed comparatively close to the lens.

Substituting for my landscape lens the symmetrical doublet, I measure its field of visibility, first full aperture and then with a small stop, and I now find that the extent of the field is not practically affected by the diameter of the stop.

Here, of course, the position of the stop being nearly coincident with the position of the nodal points, the rays make equal angles in every case.

It by no means follows, however, that a lens having a certain field of visibility is available for use with a plate, the longest diameter of which is the diameter of that field, because although rays of a certain degree of obliquity are capable of giving an image, that image may be utterly wanting in sharpness owing to the spherical and chromatic aberration of the lens for such oblique rays.

We have to consider, in other words, not merely the field of visibility, but also the field of definition.

In front of my lantern condenser I have placed a slit, the distance between the jaws of which can be varied at will, and in the focus of this powerfully magnifying Ramsden eyepiece is another slit, the distance between whose jaws admits of exact measurement by means of a scale at the side.

Remembering now that the diameter of the circles of confusion must not exceed  $\frac{1}{100}$ th inch when viewed at a distance of 12 inches, it follows that if I place the single lens so that its nodal point of emission is 12 inches from the second slit, and cause the image of the first slit projected by the lens in question to just pass through the jaws of the second, then that image will be sharp (so far as direct vision at 12 inches is concerned) if in any position of the lens it still passes through the jaws of the second slit widened to the extent of  $\frac{1}{100}$ th inch.

The eyepiece (fig. 38) is, as you see, mounted so that it can be moved right or left, and a board pivoted at  $c$  carries the lantern a graduated circle, giving the angle which the lantern may be caused to make with its original direction.

Adjusting the jaws of my second slit so that the distance between them is  $\frac{1}{100}$ th inch, I cause the image of the slit in my lantern, whose axis now coincides with that of the lens, to be formed in the focus of the eyepiece, which is itself 12 inches from the node of emission of the lens, and I then move the lantern to and fro until the image is perfectly sharp.

Now, altering the distance between the jaws of my lantern slit, I cause the image to exactly fill the eyepiece slit, and this done, I widen the jaws of the latter to the extent of  $\frac{1}{100}$ th inch.

Next causing my lantern to make an angle of  $45^\circ$ , I move the eyepiece until I perceive the image, but find that this more than fills the slit. Decreasing the angle to  $40^\circ$ , I get a similar result,



and it is only when the angle is reduced to  $10^\circ$  that the jaws of the slit,  $\frac{1}{100}$ th inch wider than before, are just filled.

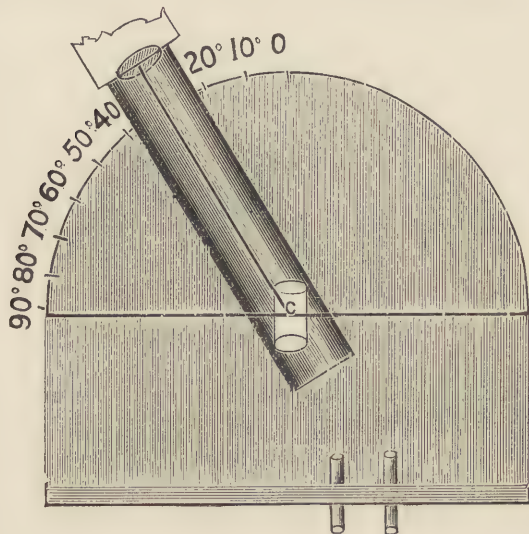


FIG. 38.—APPARATUS FOR TESTING LENSES.

Twice this latter angle or  $20^\circ$  is, then, the field of definition with the largest stop.

Inserting now the smallest stop I find that I can increase the field of definition to nearly  $60^\circ$ . Evidently I can increase it no further, for the field of visibility with this stop is  $60^\circ$ , and by using a still smaller stop I would reduce this latter.

If, however, I had made the experiment with a doublet we should have found that, other things remaining the same, the field of definition would become greater and greater up to the point when the limit of the field of visibility with the full aperture would be reached, for the decrease in the size of the stops would not in this case reduce the field of visibility, although it would increase the field of definition.

Knowing the angle of the field of visibility of a lens with any stop, and its focal length, we can easily, by graphic construction, arrive at the longest diameter of the plate it will sharply cover with that stop.

Taking as a type my single lens, in which the field of definition with the smallest stop may be taken as  $60^\circ$ , I draw (fig. 39) two

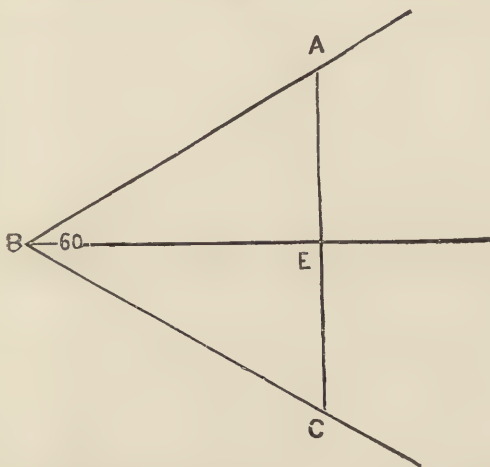


FIG. 39.—DETERMINATION OF SIZE OF PLATE COVERED BY A LENS.

lines A B, B C, making that angle with each other, and bisecting the angle so formed by the line B E, I make B E equal to the focal length of the lens, in this case five inches. Then the perpendicular A C is the longest diameter of the plate sharply covered, and direct measurement proves it to be practically  $6\frac{1}{4}$  inches. If, however, the angle had remained the same, but the focal length B E had been made greater, or conversely, if the focal length had remained the same and the angle had been made greater, then in both cases the lens would have covered a larger plate. It follows from this that the size of a plate a lens will cover varies directly as its focal length, and directly as the angle of its field of definition, but to know the exact size covered we must know both the focal length and the angle.

#### SUMMARY.

The *nodal points* of admission and emission are those points through which rays of every incidence pass.

In a *single lens* of the (usual) meniscus form, these points are practically coincident, and lie a little *behind the centre of the convex surface*.

In a *symmetrical doublet* the node of admission is in front of the stop, that of emission behind it.

In a portrait lens of the Petzval type, the node of admission is behind the stop, that of emission in front of it.

*From the nodal points all distances are measured.*

The *principal focal length* of a lens is the *distance* between the *node of emission* and the *point* (or plane) at which *parallel rays* meet.

The *principal focal length* and the lengths of any two corresponding *conjugate foci* are connected by the formula  $\frac{1}{F} = \frac{1}{f} + \frac{1}{f_1}$ , from which all distances for reducing or enlarging may be calculated.

But we must know to do this the *principal focal length* and the *position of the nodal points*.

The so-called *optical centre* of a lens coincides with the nodal points *only* when the lens is *infinitely thin*.

The *field of visibility* of a lens is the *circle of light* it casts on the ground glass when a white object, say the sky, is in front of it.

The *field of definition* of a lens is the *circle* in which all objects are in *focus*.

In *single* lenses the *field of visibility* is *diminished*, and the *field of definition* *increased* by stopping down.

In *doublets* the *field of visibility* is *unchanged*, the *field of definition* *increased* by stopping down.

*Both fields* are most conveniently *expressed as angles*.

Knowing the *focal length* and the *field of definition* of a lens, the *size of the plate* it will cover can be easily *ascertained*.

A lens of a *given focal length* may be made to include a *narrow or wide angle*, and, conversely, lenses including a *given angle* may be made of different *focal lengths*.

A *wide-angle* lens is *not* necessarily a *short-focus* one, nor a *narrow-angle* lens a *long-focus* one.

## LECTURE XI.

SPHERICAL ABERRATION AND ITS RESULTS, BAD DEFINITION, CURVATURE OF THE FIELD, ASTIGMATISM AND DISTORTION—INFLUENCE OF DIAMETER AND POSITION OF STOP UPON THESE—INFLUENCE OF DIAMETER OF STOP UPON DEPTH OF DEFINITION—THE USE AND MISUSE OF THE VERTICAL SWINGBACK.

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WE have hitherto considered only one defect to which the existence of spherical aberration in a lens gives rise, viz., the want of distinctness of the image. But there are other defects, the existence of which is due to spherical aberration, viz., curvature of the field, astigmatism, and distortion.

Causing my plano-convex uncorrected lens to project on the screen the images of a series of squares of gradually increasing size, I reduce spherical aberration by stopping down the lens to such an amount that the image of the central square is sharp, the outer image being indistinct.

Stopping down still more, the image of the second square becomes much sharper than before, and the use of a very small stop enables us to bring the images of all the squares in fairly good focus at the same time.

When the lens possessed an amount of spherical aberration just sufficient to enable the image of the central square to be sharp, the images of the outer squares were indistinct because they were formed on planes nearer the lens than that which received the central image.

Evidently, if this be true, I should be able to get a fairly sharp image by substituting for my flat screen a concave surface, and putting the matter to the test by receiving the image upon a concave cast of plaster of Paris, you see that the result bears out the explanation which theory enabled us to arrive at. You will see from this the reason of the name given to this defect, viz., curvature of the field, it being necessary, in order to obtain the greatest possible amount of sharpness with a lens possessing some spherical aberration, to receive the image, not on a flat, but on a concave, surface.

With the lens used in the ordinary way, the want of sharpness of the outer squares is due to the fact that the axial rays are more bent than the marginal ones, and by stopping down, or by using a correcting lens, we reduce the bending of the marginal rays to a smaller amount, and so diminish the curvature of the field.

Causing my lens to once more project an image of the series of squares, I stop it down until the central image is just sharp, and

then rack it out until the image of the marginal square is as sharp as we can get it.

If you now examine the degree of sharpness of this image, you will at once perceive that it is by no means so great as that of the central image with the lens in its original position.

Hence, even if we had used a concave surface to receive the images, an equal amount of all-round sharpness would not have been obtained.

This second defect is termed astigmatism, and a reference to fig. 40 will enable us to understand the cause of it. Taking the rays  $A B$ ,  $A C$ ,  $A C^1$ ,  $A B^1$  concerned in the formation of the central image, fig. 40, it is easy to see that  $A B$ ,  $A B^1$  and  $A C$ ,  $A C^1$  are

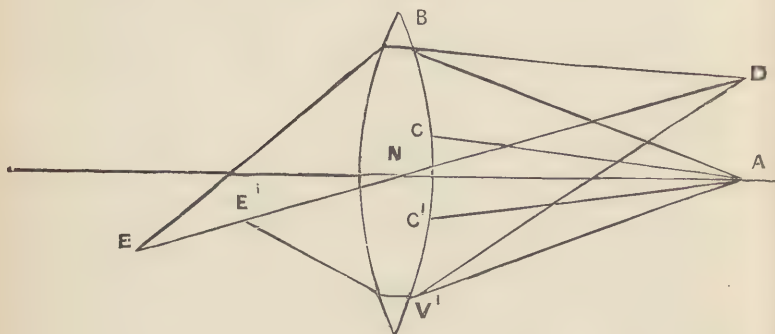


FIG. 40.—CAUSE OF ASTIGMATISM IN A LENS.

symmetrically situated with respect to the principal axis  $A N$ . Now, provided we stop down sufficiently to cause the pair of rays  $A B$ ,  $A B^1$  to be bent to practically the same extent as  $A C$ ,  $A C^1$ , we will increase the sharpness of the central image. But if we take a point  $D$ , representing the marginal squares of the object, then it is easy to see that the ray  $D E^1$  will be more than  $D E$ , the latter meeting the principal axis at a point  $E^1$  on the principal axis further from the lens than the point  $E$ , at which the ray which is most bent meets it.

Hence, although we may have caused  $A B$  to be bent to the same degree as  $A C$ , we shall still have this unequal bending of  $D E$  and  $D E^1$  to contend with, and it is evident that although by stopping down still more we can decrease the distance  $E E^1$  we can never cause these two points to coincide, owing to the fact that the lines  $D E$ ,  $D E^1$  are not symmetrically placed with respect to the prin-



cipal axis of the lens. We put the matter in other words by saying that the focal length of the lens measured along the secondary axis  $D D^1$  is different to its focal length measured along the principal axis  $A E$ .

I now again project the image of the squares on the screen, using a sufficiently small stop, which you will observe is placed between the lens and screen, to reduce curvature of the field and astigmatism to a small amount, and I will ask you to notice that what should be a vertical side of the outer image is rendered by a line curving inwards, the other sides being similarly bent. The cause of this pincushion distortion, as the result is called, is rendered evident by fig 41.

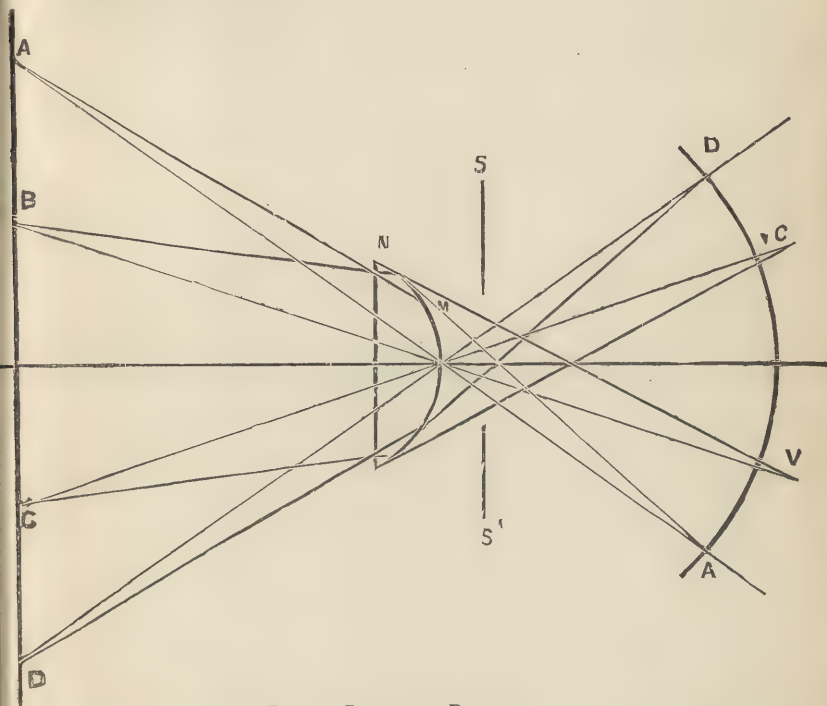


FIG. 41.—PINCUSHION DISTORTION.

Here  $A D$ , the extremities of one of the outer vertical lines, form images at  $A D$  and  $C B$ , the portions of the same line near the centre at  $C B$ .

The images A D are formed, however, on a plane nearer the lens than that which receives the images C B because the rays concerned in the formation of the former image passing through the margins of the lens are more bent than the rays concerned in the formation of the latter images, which pass through the lens nearer its centre.

As rays occupying positions between A B, C D are bent to intermediate degrees, the same being true of rays between B M, C M, we see that the straight line A B C D will be represented by the curve A B C D.

Altering now the position of my stop by placing it between the lens and object you see that distortion, although still present, assumes the opposition or barrel shaped form, vertical lines on the margins being rendered as lines curving outwards. The cause of this is shown in fig. 42. With the stop in this position the rays

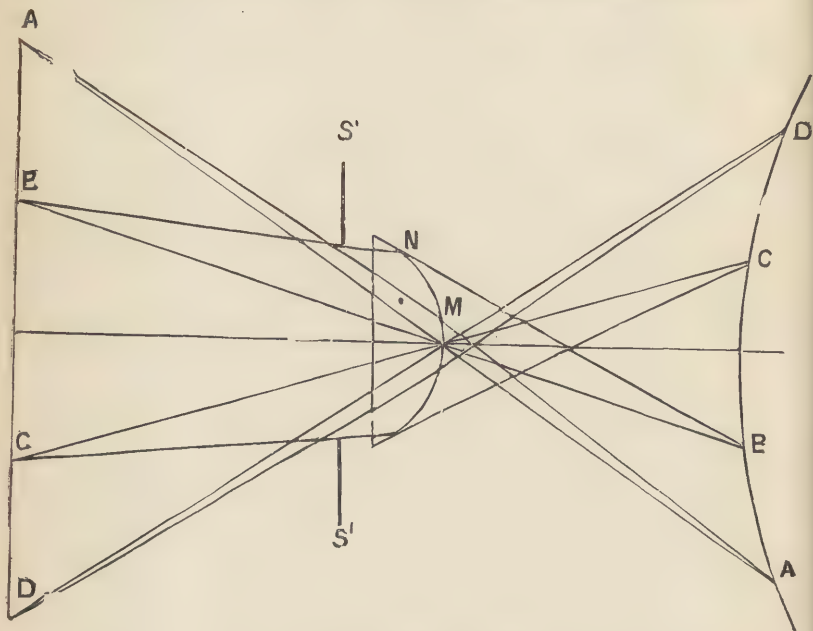


FIG. 42.—BARREL DISTORTION.

concerned in forming the images of A and D are less bent than those concerned in forming the images of B C, because the former

rays, owing to the position of the stop, now pass very near the nodal point O, and are consequently less bent than the rays proceeding from B and C, which meet the lens at its margins.

Owing to the fact that the appearance of a picture in which barrel-shaped distortion occurs is less objectionable than that of one in which the lines are curved in the opposite sense the stop is in single lenses always placed in front.

Evidently by employing two lenses with a stop between the curvature of the straight lines in one sense caused by the stop being behind the first lens might be made to find its exact counterpart in the curvature in the opposite sense caused by the stop being in front of the second lens, and provided the position of the stop and the foci of the lenses were suitably chosen we should then have a compound lens which would not distort at all.

Bringing now my stop nearer the lens, you see that by so doing I diminish the amount of distortion, but I diminish at the same time the definition of the marginal square.

A reference to fig. 42 will show the reason of the reduction in the amount of distortion.

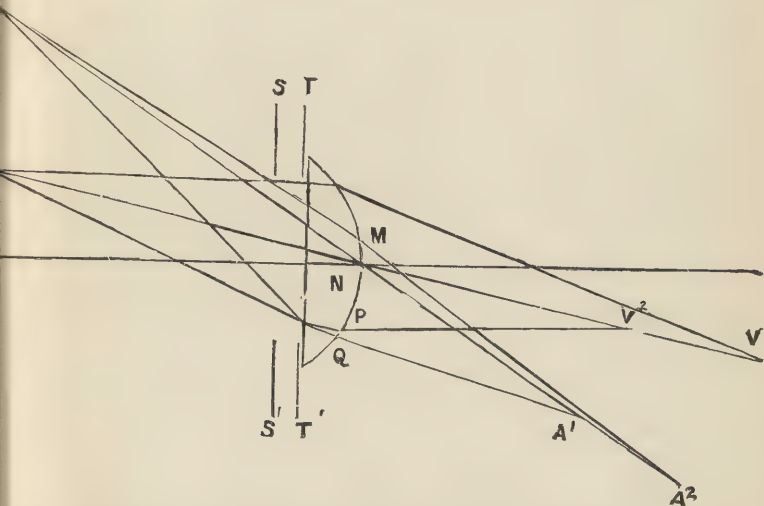


FIG. 43.—INFLUENCE OF POSITION OF STOP UPON DISTORTION AND CURVATURE

If the stop, instead of being placed as shown, had been put, say, in contact with the lens, then evidently the rays M A, M D would

have been more bent than at first because they would now meet the lens at a greater distance from its nodal point O, and since this alteration in the bending of the rays from A and D would not be accompanied by any alteration in the degree of bending of the rays C and B, it follows that the points A and D would fall on a plane more nearly coincident with that which received the images C and B.

So far, then, as distortion is concerned, placing the stop in contact with the lens reduces it to a minimum, and this would be the best position for it, were it not for the fact that in this position of the stop the sharpness is at a minimum.

A reference to fig. 43 will make this clear. Here, with the stop at S S<sup>1</sup>, the ray A M meets the secondary axis at A<sup>2</sup>, and the ray A G at A<sup>1</sup>, the distance A<sup>1</sup> A<sup>2</sup> measuring the want of definition.

Again, the ray B A meets the secondary axis at B<sup>1</sup>, and the ray B P at B<sup>2</sup>, the distance B<sup>1</sup> B<sup>2</sup> again measuring the want of definition.

If now the stop be placed at T T<sup>1</sup> then the ray A M will meet the lens nearer its margins, and being consequently more bent than before will cut the axis at a point nearer to A<sup>1</sup> than the former point A<sup>2</sup> at which it cut the same axis, making the distance A<sup>1</sup> A<sup>2</sup> less than before. But although we have by altering the position of the stop altered the direction of the ray A M, we have not altered the directions of B N, B P, hence it would be now impossible to so place the screen that the image between B<sup>1</sup> B<sup>2</sup> would be of exactly the same degree of sharpness as that between A<sup>1</sup> A<sup>2</sup>.

Clearly we can find a position for the stop at a certain distance in front of the lens such that A<sup>1</sup> A<sup>2</sup> is the same as B<sup>1</sup> B<sup>2</sup>, and then we can bring both points into focus at once, but this position is not the one at which distortion is at a minimum.

In single lenses the stop is, therefore, placed at a certain distance in front of the lens, in consequence of which distortion is present. As, however, this is not very perceptible if the lens is fairly well corrected for spherical aberration at the margins of the plate covered, no evil effects attend the use of such lenses, for even architectural subjects, provided we take care that the angle included by the object photographed is only a fraction of the angle which the lens will sharply cover.

In ordinary views, however, in which there is a foreground and distance, we do not deal, as we have hitherto supposed, with an object in a single plane, but with objects in several planes, one behind the other, and the images of these planes which pass through a series of conjugate points should be received not on one but on a series of screens placed at corresponding conjugate distances behind the lens.

If we content ourselves with having the distance in sharp focus, then the foreground will be out of focus, because we receive it on a plane which is too near the ground-glass.

If sharpness only is what we look for, then the vertical swing back of the camera gives us a means of arriving at what we want,

as a consideration of fig. 44 will show. Here (fig. 44) if the ground glass  $G G^1$  is vertical, and we focus for an object  $D$  in the far distance, the image of that object will be formed at  $D^1$ . But

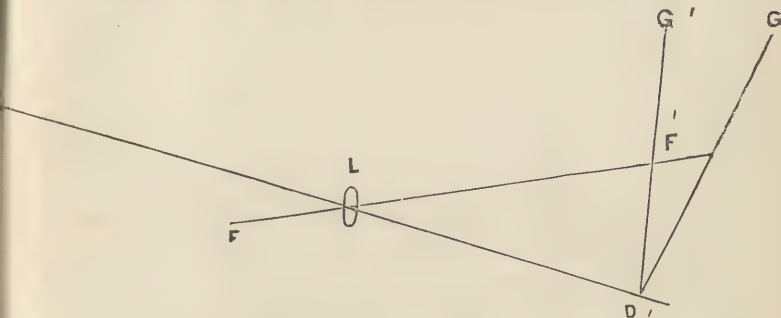


FIG. 44.—POSITION OF GROUND GLASS AS INFLUENCING SHARPNESS AND PERSPECTIVE.

evidently the image of an object  $F$  in the foreground should theoretically be formed at  $F^1$ , further off than the ground glass, and we cannot, therefore, with the lens at full aperture have both images sharp at once. But if we tilt the ground glass into the position  $G' G'^1$ , then it is evident that, without altering the distance  $O G$  between the ground glass and  $O$ , we have caused the image at  $F^1$  to fall on the ground glass, upon which, therefore, both points will be depicted with equal sharpness at one and the same time.

This, then, might seem a perfect means of causing the image-planes of corresponding object-planes at different distances from the lens to all fall on the ground glass, and so it would were we merely dealing with a series of points, and were utterly unconcerned as to whether or not the ratios between their distances from each other in planes parallel to the ground glass were rendered by corresponding ratios between the distances of their images on the ground glass. But this would evidently be false reasoning, for upon the correct rendering of these ratios depends the truth of the image to nature.

Causing the image of my series of squares to fall upon this piece of ground glass, which can be tilted more or less, you see that the squares are rendered as squares only on condition that the ground glass is parallel to the plane of the object. If keeping the object vertical I tilt the top of the ground glass towards the lens, then the image is narrowed at the top, whilst if I tilt the top of the ground glass from the lens the image is narrowed at the bottom. If, then, the object is vertical, the ground glass must also be vertical if a truthful picture is sought. Now, tilting up my lantern, you see



that the squares ruled on the piece of glass in front of the condenser seem to converge at the top, and once more receiving the image on my vertical ground glass you see that it is again true to nature, the object the lines of which seem to converge being rendered as an image whose lines actually converge. It follows, therefore, that to get a representation of any object *as the eye sees it*, the ground glass of the camera must always be vertical.

Now, an examination of fig. 44 shows that to get sharpness we must place the ground glass not vertical, but making an angle with the horizon. If we tilt it so as to get sharpness then the lines must converge at the top of the resulting picture to a greater extent than they seem to do when the object is viewed by the eye, the result being in buildings distortion, and in ordinary views a lengthening out to an inordinate degree of the distance between planes near the camera and others further from it.

This falsification of the image is particularly evident in photographs of mountains taken by those who aim at sharpness only, and use the swing back so as to get it.

To illustrate this point I project upon the screen two photographs of Snowdon, one taken with the ground glass vertical, the other with the top swung from the mountain, and although the latter is very much sharper than the former, there can be no question but that the sharp photograph is an utter travesty of nature, the towering peak appearing dwarfed to a hillock of pigmy size.

We are not, however, very fortunately, totally depending upon the ground glass for sharpness, and this leads us to consider what

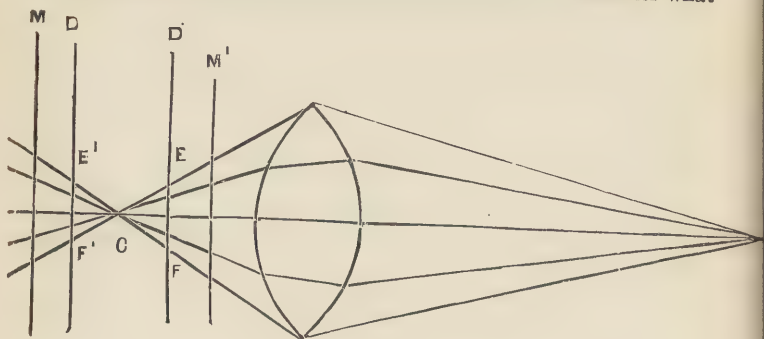


FIG. 45.—DEPTH OF DEFINITION.

is called depth of definition. In fig. 45 let O represent an object and C the point at which an image of maximum sharpness is

obtained. Then, since we have agreed to call all images sharp, the diameters of the circles of confusion of which do not exceed  $\frac{1}{100}$ th inch, we may, without, as we say, altering the sharpness, move the ground glass to D or D<sup>1</sup>, the diameters of the circles E F or E<sup>1</sup> F<sup>1</sup> equalling  $\frac{1}{100}$ th inch.

Now it is easy to see that if we reduce the aperture of the lens to half its former amount we reduce the diameter of E F or E<sup>1</sup> F<sup>1</sup> in like proportion, and we express this by saying that the depth of definition varies inversely as the diameter of the stop we use.

To obtain depth of definition we have recourse, therefore, to a small stop, and as this depth of definition means increased sharpness, the employment of small stops is the only correct method of bringing object-planes at different distances from the lens in focus at one and the same time.

#### SUMMARY.

*Spherical aberration is the cause of curvature of the field, astigmatism and distortion.*

*Curvature of the field* would entail the use of a *convex* screen to receive the *flat* image.

*Astigmatism* is caused by the *focal length* along the *principal axes* being *different* to that along the *secondary axes*.

A lens free from *spherical aberration* along *all its axes* would be free from *curvative* and *astigmatism*.

*Stopping down* diminishes *spherical aberration* and its attendant evils by producing *greater depth of definition*.

*Depth of definition* varies *inversely* as the *diameter* of the *stop*.

*Object-planes* at *different distances* in front of the lens require *picture-planes* also at *different distances* behind the lens, an *object-plane* at one *conjugate focus* requiring a *picture plane* at the corresponding *conjugate focus*.

The *misuse* of the *swing back* enables us to get this, but the *representation* of objects as *seen* by the *eye* requires the *ground glass* to be *vertical* in every case.

Hence to obtain *sharpness* we must *rely* not upon altering the position of the ground glass but *upon the stop*.

## LECTURE XII.

TYPES OF PHOTOGRAPHIC LENSES—THE SIMPLE LENS—THE LANDSCAPE OR SINGLE CEMENTED LENS—THE DOUBLET OR PAIR OF CEMENTED LENS—RECIPROCITY OF LARGE APERTURES AND SMALL DEPTH OF DEFINITION—THE PORTRAIT LENS—HOW TO MAKE PHOTOGRAPHS TRUE TO NATURE.

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IT will be convenient at this point to briefly pass in review the chief types of photographic lenses, and the uses to which they should respectively be put. We must begin by clearly understanding that what we require a lens to do is a theoretical impossibility, for a lens can only depict one object-plane at a time, everything else being out of focus. But owing to the fact that the eye at the distance of normal vision cannot distinguish a mathematical point from a circle  $\frac{1}{100}$ th inch in diameter, we can in practice cause objects in different planes to form images of sensibly equal sharpness.

Taking as type of a simple or uncorrected lens this plano-convex lens of crown glass, we have learnt that it possesses both chromatic and spherical aberration, with all their attendant evils. Stopping-down such a lens, however, we reach a point at which a fair amount of visual sharpness is obtained, and the increased depth of definition which the lens possesses enables it to produce a negative on a plate placed at the focus of the visually brightest rays (D line) differing but little in sharpness from the one which would have been produced had we placed the plate nearer the lens so as to coincide with the focus of the blue rays (G line).

Evidently the higher the refractive index of the material of the lens the less the amount of stopping-down required.

Owing, however, to curvature of the field, the field of definition of such a lens would be but a small fraction of its field of visibility, and the more we stop down the more we reduce this latter. By shortening the focus of the lens we reduce the difference between its foci for the D and G lines, and we consequently reduce the amount of stopping-down requisite to cause the foci for these two lines to practically coincide.

It follows from all this that by using a lens of a material—say quartz—of a high refractive index, and by making it of a sufficiently short focus, we can make it cover a small-sized plate with a fair degree of sharpness.

But of course the more we stop it down the slower it becomes. The aim of the lens maker is, therefore, to construct a lens

covering at large aperture a plate of a considerable size, and this object he attains by completely correcting chromatic and spherical aberration for axial rays by cementing a flint and crown lens together, as in fig. 46. Such a combination is, how-

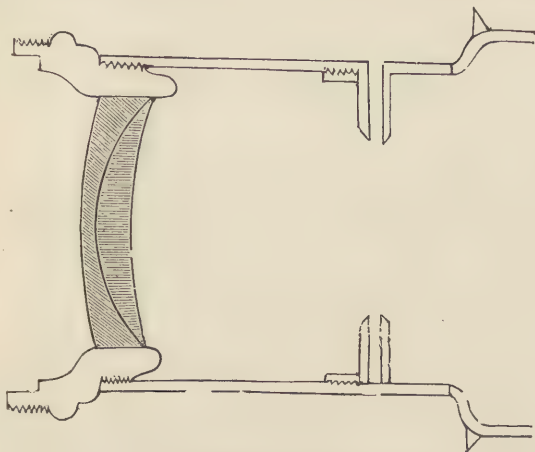


FIG. 46.—THE SINGLE ACHROMATIC LENS.

ever, uncorrected for rays along its secondary axes, with the result that if we wish to make it cover a surface of any extent, or wish to use it with very near objects, we must increase its depth of definition by stopping it down. Clearly, however, since spherical and chromatic aberration are corrected for axial rays, a much larger stop will give the same amount of definition as a smaller stop in an uncorrected lens of the same focus.

Comparing the two lenses, it will at once be apparent that we have in the cemented lens one covering (comparatively) a large surface with a large aperture.

But we remember that the position of the stop determining the maximum amount of sharpness is a position which is favourable to distortion, hence such lenses distort straight lines more or less. If, however, we combine two of them, as in fig. 47, we obtain a rectilinear lens in which distortion is absent. In this case the lenses being turned in opposite directions the greater bending of the marginal rays towards the axis by the front lens is corrected by the back lens bending the same rays to an equivalent amount from the axis, with the result that spherical aberration may be more completely corrected along secondary axes, and the lens

will usually therefore cover sharply a larger surface than a single lens of the same focus and aperture.

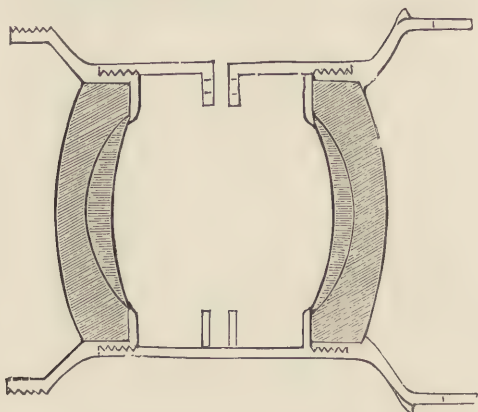


FIG. 47.—THE DOUBLET LENS.

Again, since the size of the stop does not alter the extent of the field of definition, it is possible, by using a very small stop, to make the lens cover a much larger surface than would be possible, owing to the reduction of the field of definition, had a single lens been employed. We can therefore make such lenses of very short focus.

Comparing the depth of definition of a lens of this type with a single one, we see that to cause the single lens to cover the same extent of surface as the rectilinear used full aperture we must stop down the single lens, but having done so the latter lens now possesses greater depth of definition because it is stopped down to a greater degree.

For equal fields of definition the single lens is more rapid than the doublet, but since this gain in rapidity is accompanied by a loss in depth of definition we see that these two qualities are diametrically opposed to each other.

Single lenses and rectilinears of the type just alluded to are intended, for reasons that have been already pointed out, for relatively distant views, the rays reflected from which are sensibly parallel.

When, however, we have to take portraits, it is evident that we must use a different type of lens, for the reflected rays are now very divergent.

To put the matter in other words, we may say that a lens



sensibly free from spherical aberration for distant objects is over-corrected for near ones, and such a lens, although it might depict with absolute sharpness all objects in a plane one hundred feet from it, could no longer depict the same objects if that plane were distant only ten feet from the lens.

We require, in fact, in a portrait lens one fulfilling conditions quite different to those which a view lens fulfils, for we require that its spherical and chromatic aberration shall be corrected along all axes, and we at the same time require the lens to be very rapid, *i.e.*, to work with a large aperture.

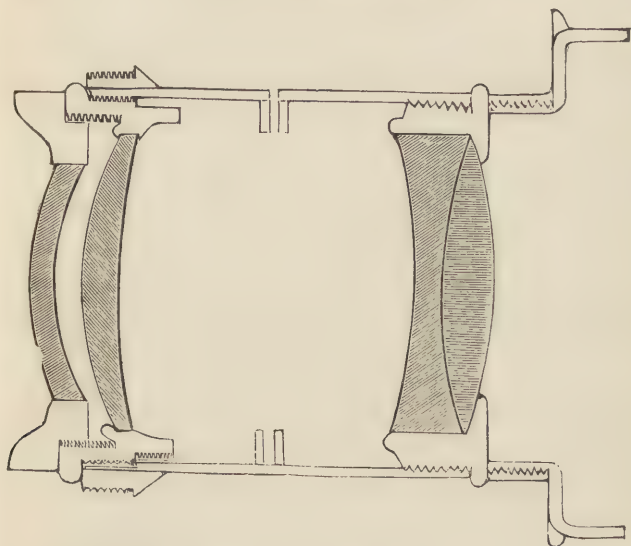


FIG. 48.—THE PORTRAIT LENS (PETZVAL-DALLMEYER TYPE).

In the portrait lens (fig. 48) these conditions are fulfilled by an intelligent choice of materials, &c. But it is quite clear that in all such lenses the correction of the aberrations along secondary axes can only be true when these secondary axes make not more than a certain maximum angle with the primary one.

It is for this reason that with all such lenses the sitter must be placed at not less than a certain minimum distance, the lens being said to work at 12 feet, 20 feet, etc., as the case may be. Used at a greater distance, the lens still gives a sharp image, but at a lesser one the image is wanting in sharpness for the reasons just pointed out.

Of course, the portrait lens, like the rectilinear, possesses little or no depth of definition, and is consequently, when employed in the ordinary way, quite useless for depicting objects in different planes at one and the same time.

If the lens has to be employed for groups, we must either stop it down, or increase its spherical aberration (if it is a portrait lens of the Dallmeyer type) by increasing somewhat the distance between the uncemented lenses of the back combination.

It may, at first sight, seem strange that increasing the spherical aberration should increase the depth of definition, but the experiment I am about to make will prove that such is really the case.

Placing this gas flame in front of my uncorrected plano-convex lens, I cause its image to be formed on a sheet of ground-glass in front of the lens, and focussing so as to get the maximum possible sharpness, you perceive that I can move the gas flame through nearly an inch without causing the sharpness to diminish. Now stopping down my lens considerably I repeat the experiment, and, as you see, the distance through which I can now move the gas flame without impairing the sharpness is reduced to less than a quarter of an inch. In fact, with a perfectly corrected lens, there would be only one distance at which an image possessing the greatest possible sharpness would be formed, and the slightest variation in that distance would cause this sharpness to be quite lost.

We learn from this that, although a lens possessing some spherical aberration does not give at any point an image as sharp as one possessing none, nevertheless the all round sharpness given by the former lens is greater than that given by the latter one, a result which, traced to its source, evidently means that in the one case we have some very sharp plane for comparison, whilst in the other case the absence of such a plane makes the eye incapable of estimating so well the actual want of sharpness.

Having now learnt the leading properties of photographic lenses, we will conclude this part of our subject with an enquiry into the way in which lenses should be used in order that they may give what should be the aim of all good photography, a picture true to nature. In what follows it must be understood we are dealing only with the picture as it appears on the ground glass: the correct rendering of colour in monochrome and the correct development of the negative forming part, not of the optics, but of the chemistry of photography.

We have learnt that every lens has a certain field of visibility and a certain field of definition. Now the lens of the eye has also a field of visibility and of definition, and evidently a photographic lens will render a view truthfully when its fields coincide with the corresponding fields of the eye itself.

As regards the field of visibility of the eye most authorities agree that it cannot be made to exceed  $60^\circ$  without some movement of the head, and its field of definition is evidently much

more restricted, never exceeding, in all probability, an angle of  $10^\circ$ .

Now, when our aim is to convey a certain impression to the brain by means of the eye, we unconsciously select our standpoint, so that the object or objects which constitute that impression shall subtend at the eye the given angle of  $60^\circ$ .

Supposing, for instance, that at a certain distance in front of us there was a house, with a lake on one side, and a clump of trees on the other. Then, if our object was to form a mental picture of these three things, we would alter our position further or nearer from them until all three were included in the image formed on the retina. If our object was to form a mental picture of the house only, then we would approach nearer to it until, in fact, it alone subtended the requisite angle.

It follows, therefore, that what would be the best point of view for the lake, house and trees would not be the best point of view for the house only, the best point of view for a given amount of subject being selected, in fact, with reference to the eye alone.

Having selected our point of view, say, for the lake, house and trees in the manner just indicated, we must now ask ourselves what we should do in order to make a truthful photograph of it.

Before answering this question, it may be well to point out that size only has nothing to do with the truth or the reverse of a picture. Supposing, for instance (fig. 49), we placed upright, at a distance of 100 feet in front of the eye, a pole A B 26 feet above the ground, making a mark C on it at the level of the eye. Then it would be quite easy, by placing another pole A C B, only seven feet high, nearer the eye at E, to find a position at which C B gave the same impression as C B. Clearly, therefore, a series of poles of gradually decreasing heights placed between C and C would all

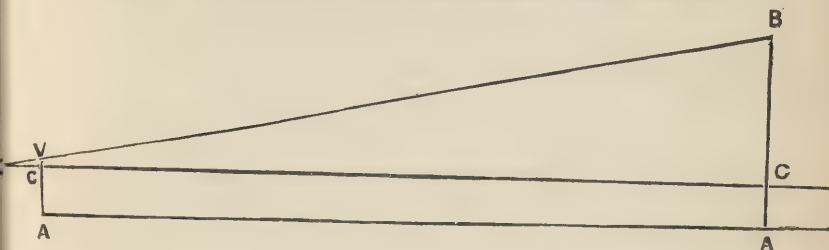


FIG. 49.—TRUE PERSPECTIVE UNINFLUENCED BY SIZE.

give identical mental impressions provided they were viewed from the same standpoint, or, in other words, provided that the distance between the eye and each pole varied directly as the height of the latter, for in our diagram it is easy to see that  $BC : EC :: EC : EC$ .

Our standpoint being then selected, we may take any lens which will give on a plate of any size a picture including just what we see, and that picture will be true to nature (the lens being properly stopped down) when viewed at a distance equal to that between the ground-glass and the nodal point of emission of the lens with which it was taken.

In connection with this latter point it may be well to remark that the minimum distance of distinct vision is 12 inches, *i.e.*, the eye cannot conveniently view an object at a smaller distance.

If, then, our picture is formed at a smaller distance than 12 inches, we must enlarge it to such a degree as to make the distance at which it must be viewed equal to at least 12 inches. We may, of course, make the enlargement as big as we please, but if we do so we must remember that it must be viewed at a correspondingly great distance.

We made you remember the reservation that the lens must be properly stopped down. What is the meaning of this?

In every picture there is an object of interest, *the* object which the eye sees most distinctly when looking at that picture. Now, this object will never subtend at the eye more than an angle of  $10^\circ$ , that being the field of definition of the eye, and it follows, therefore, that just as the extent of our lens field of visibility was determined with reference to the eye alone so must the eye also determine the extent of our field of definition.

We have in the stops a means of increasing the angle of this field, and we must evidently stop down the lens so that it equals  $10^\circ$ . It does not, however, follow that the same stop will answer at every distance, for the extent of the field of definition depends, as we remember, upon the extent to which spherical aberration for oblique rays has been corrected. The greater the distance, in other words, between the lens and the object the greater the field of definition, and less stopping-down will be then required to bring this to  $10^\circ$ , owing to the fact that the greater the distance the more parallel the reflected rays become.

Having, then, selected our point of view with reference to the eye alone, we must use a lens which at that distance gives a picture including just what the eye sees, and stop it down so that the field of definition all round the principal object subtends an angle of  $10^\circ$ . This done, we may be nearly sure that the resulting picture will be as true to nature as optics can make it, provided always the eye be placed, when viewing a print representing it, just as the lens was placed when forming its image on the ground-glass or sensitive plate.

It often happens, however, that objects which are not the ones of interest happen to fall on the same plane as the object of interest itself.

In the given example, for instance, it might happen that some of the trees to one side of the house would be as sharply depicted as the house itself. The eye, in other words, focusses for a circle,



*i.e.*, its field of definition, all objects outside that circle, whether in the same plane as it or not, being indistinct. The lens, on the other hand, is so constructed that, although stopped down so as to include a given circle of definition, it may render other objects quite outside that circle as sharply as objects included in it if the objects outside the circle of definition happen to coincide with the plane of that circle.

This fact might, at first sight, seem an unsurmountable difficulty, but it is not so, for evidently if we made the original picture on a relatively small scale, and took care that every or nearly every portion of it was equally sharp, then we could, by subsequently enlarging that small negative, cause the resulting enlargement to possess any field of definition we please.

This method, then, *viz.*, the production of small and perfectly sharp pictures which are subsequently enlarged in accordance with the principles just laid down, is probably the only one which would at all times render a view exactly as the eye sees it.

#### SUMMARY.

*A simple uncorrected lens may be made to yield sharp pictures if a sufficiently small stop is used with it. This stop diminishes, however, the field of visibility very considerably.*

*If, then, we want a comparatively large extent of surface to be covered we must make the uncorrected lens of long focus, and so increase its depth of definition to such an extent as to permit of the employment of a comparatively large stop.*

*In the single cemented lens aberration is corrected, not by stops, but by suitably choosing the materials and curves of the two lenses. It will, therefore, cover a comparatively large surface with a large stop, although placed at a short distance from the ground-glass, i.e., although of short focus.*

*Single cemented lenses usually distort.*

*In lenses of the doublet type there are a pair of suitably chosen corrected lenses with the stop between. Spherical aberration along secondary axes being now better corrected owing to the way the lenses are turned a larger extent of surface can be sharply covered.*

*Portrait lenses are corrected with special care, and so cover with excellent definition a small extent of surface at full aperture.*

*The larger the aperture the less the depth of definition.*

*Truth to nature should be the aim of photography.*

*The image of any object subtends on the retina of the eye an angle of 60 degrees.*

*The minimum distance of distinct vision is 12 inches.*

*To select the correct point of view the camera must be so placed that the eye placed at the same point sees the whole of the view it is desired to depict.*

*This done, a lens is selected which projects on a plate of the required size, just the amount of view seen by the eye and no more.*

*If the distance between lens and plate is 12 inches we must view*



the resulting prints at 12 inches. If the *distance* is *less* we must *enlarge* them so as to enable them to be *conveniently viewed*.

If the *distance* between *lens* and *plate* is *greater than 12* inches we must view the prints at whatever that distance may be, or *reduce* them and view them at 12 inches.

A *converging* or *diverging* lens used to view the prints taken with the *too short* or *too long* focus lenses will cause them to give a correct mental impression.

## LECTURE XIII.

THE MOLECULAR THEORY OF MATTER AND ITS PROOFS—PHYSICAL EXPLANATION OF TRANSPARENCY—RELATION BETWEEN THE TEMPERATURE OF A BODY AND THE RATE OF VIBRATION OF ITS MOLECULES—EXPANSION THE USUAL RESULT OF A RISE IN TEMPERATURE—DISTINCTION BETWEEN MOLECULES AND ATOMS—DENSITIES—ATOMIC WEIGHTS AND WHAT THEY SIGNIFY—MOLECULAR WEIGHTS—CHEMICAL EQUATIONS.

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THE wave theory in optics finds its counterpart in chemistry and in chemical physics in the molecular-atomic theory of the construction of matter. To explain the phenomena to which light in the abstract gives rise, we assumed, as you have learnt, the existence of the ether, and explained those phenomena by the motions of its particles. Similarly, we refer the various changes which matter undergoes to the positions, changes of position, or motions of its finest particles.

The term matter here refers to whatever can be weighed, and taking as a type of matter this piece of silver, evidence of the clearest kind goes to prove that it is made up of a large, but by no means infinite, number of minute particles termed molecules, each of which admit of further subdivision into still smaller particles called atoms.

I have between these two plates of glass a very thin silver leaf, and, placing the whole in front of the condenser of my lantern, you perceive that, although a lump of silver is opaque, a sufficiently thin film of the same material transmits bluish light.

Now, if the silver were continuous throughout, *i.e.*, if it was not made up of independent particles not in absolute contact with each other, it is inconceivable that it should transmit light at all, for we know that the ether is essential to the transmission of light, and if no space existed between the finest particles of the silver, the ether would necessarily be excluded.

Since, then, light is transmitted, we are driven to the conclusion that the silver is actually made up of particles at a certain distance from each other, and that this is true of every substance is borne out by the well-known fact that the opacity or transparency of a substance depends upon the thickness of the film of it used for the experiment. Some materials, like silver, must exist in very thin films to transmit light; others, like glass and water, transmit light through comparatively thick films, but are as opaque as silver in films of a sufficient thickness, and this being the case, we conclude that any substance ordinarily opaque would transmit light

if we had it in our power to experiment upon a sufficiently thin film of it.

Now, although at first sight it might seem as if the molecules of a substance were at rest, there is good reason for believing that this is not usually, at least, the case, but that the molecules are vibrating.

Placing the piece of silver on this small anvil, I strike it a succession of blows with a hammer, and, although it was quite cold at first, my fingers are now made conscious of the fact that the blows it received have resulted in warming it.

The molecules of the silver were at first in a state of comparative rest, but the blows which I gave the material set them in more energetic motion, with the result that they started ether waves of small frequency, and gave rise in consequence to the sensation of heat.

But heat and cold are merely comparative terms, and it follows from this that before I placed the silver on the anvil its molecules must have been vibrating, but so slowly as to give rise to ether waves, the same in period as those already present in the room, the substance being, as we say, at the same temperature as the air, the hand, and other surrounding substances.

These two wooden balls, separated from each other by a coiled steel spring, illustrate two contiguous molecules of the silver. If the substance was at the theoretical temperature of absolute zero, then the balls as they are at present, viz., at rest, would truly represent the two molecules, but to cause them to represent the actual state of affairs I must make them vibrate.

Evidently, if I strike the top ball a slight blow it vibrates with a small velocity, representing a comparatively low temperature, but if I increase the force of the blow I cause it to vibrate with a greater velocity, representing a higher temperature.

If I could cause the ball to vibrate at the same rate as the ether waves, the effect of which my fingers appreciate as heat, then the mass of matter represented by the two balls would be spoken of as hot.

Since increased molecular vibration results in rise of temperature, the converse should be true, *i.e.*, that a rise in temperature is accompanied by increased molecular vibration, and as we have already proved this rise in temperature to result in increased ethereal vibration, we can now see what a close connection exists between the vibrations of the molecules of a substance and those of the ether waves to which those molecular vibrations give rise.

Now, in most cases, a rise in temperature is accompanied by an increase in the bulk of the substance. Causing an electric current to pass through this fine platinum wire stretched across the table, you see that the wire glows and sags more or less, and the same thing can be proved true of a silver wire by passing the Bunsen burner beneath this silver wire stretched between two supports,

when you see that the index moves, showing that the wire has become longer than before (fig. 50).

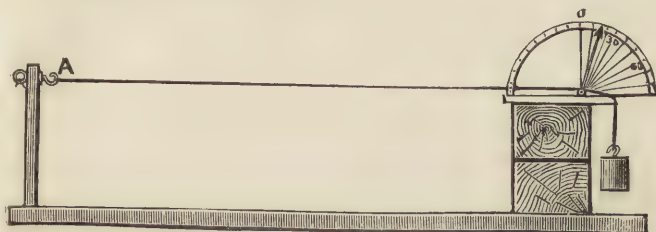


FIG. 50.—RISE IN TEMPERATURE PRODUCING EXPANSION.

Comparing, then, the piece of silver when cold with the same piece when heated, we see that in the latter case its molecules are further apart and vibrating more rapidly than in the former case. I have in this tube some silver in a very fine state of division, such as we obtain it when solutions of silver nitrate and of ferrous sulphate are mixed, and you see that it is in this state a brownish powder, devoid of that glistening or lustrous appearance so characteristic of metallic silver in its usual condition. I have here a plate of copper coated with silver by galvanic action, and you observe that the chalky-looking deposit is again very different from silver as we usually meet it.

Grinding in a mortar the brownish powder, whilst my assistant polishes the chalky deposit with a piece of chamois, you are made cognisant of the fact that the two things were really silver and nothing else, for in both cases the characteristic lustre has been restored.

In silver in its usual state the molecules are, in fact, arranged in one way, and in the brown powder or chalky deposit in another, but friction has, in the latter cases, made them revert to the usual arrangement, and when that is done the lustre and brilliancy re-appear.

We might, in fact, explain the result by saying that just as by differently arranging the three letters *a r t*, we can get three distinct words, *art*, *tar*, and *rat*, so a different arrangement of the molecules in the mass of any substance may give us, not three distinct substances, but the same substance affecting our senses in three distinct ways.

Molecules, then, by their rate of motion, distance apart and arrangement determine what we call the physical properties of the mass of which they form part.

A molecule is not, however, the smallest portion of matter of which we have any conception.

Pouring some nitric acid over a piece of silver contained in this glass flask abundance of red fumes are given off, and in a short

time the solid metal completely disappears, having, as you know, become converted into a solution of silver nitrate.

Now, no one looking at solid silver nitrate, not knowing what it was, would imagine for a moment that metallic silver and nitric acid had to be taken to make it, nor could anyone possibly mistake the semi-transparent crystalline solid for either a lustrous metal or a colourless liquid.

Since in the silver nitrate the characteristic properties of metallic silver are lost, we are justified in saying that it contains silver, not as molecules, for if it did the eye would make us cognisant of the fact, but as finer and smaller particles, which we call atoms.

The molecule, then, admits of sub-division, and this sub-division, resulting in the formation of a new substance possessing properties quite distinct from those of either of the original substances, constitutes chemical change.

From silver alone, as you of course know, I cannot obtain two other distinct substances, but by heating silver nitrate I can obtain metallic silver, and by distilling it with sulphuric acid I can obtain nitric acid.

Substances like silver are elements, and in these the atoms present in each molecule are similar in kind, whilst substances like silver nitrate and nitric acid are compounds, the atoms in each molecule being now dissimilar in kind.

We are acquainted with between sixty and seventy elements, but the number of possible compounds is of course exceedingly large.

By mutual agreement chemists denote an element by what is called its symbol, which is the first letter or letters of its English, or in some few cases its Latin, name.

Thus, we denote silver by Ag, chlorine by Cl, bromine by Br, and so on; and by further mutual agreement the symbols as thus written indicate not merely the name of the element, but also one atom of it.

Some of the elements are lighter than air, others heavier than it.

In this jar I have some inflammable hydrogen gas, and holding it over this second jar as if I were actually pouring the hydrogen *upwards*, I then apply a light to the mouth of the first jar, when, as you see, no hydrogen is there, but applying the light to the second the slight detonation proves that the hydrogen has actually been poured upwards owing to the fact that it is lighter than air.

Now, taking a jar of greenish yellow chlorine, I hold it over an empty jar just as if I were pouring water from one to the other. Plunging a taper into the first jar, you see that it burns as in air, but now plunging it into the second the smoky flame shows that the chlorine has passed downwards. We have here, then, a gas which is heavier than air.

Chlorine being heavier than air must, *à fortiori*, be heavier than hydrogen. If, in fact, we took two vessels of the same capacity, and filled one with chlorine and the other with hydrogen, we should



find that one weighed practically 35 times more than the other. We say, therefore, that the comparative densities of hydrogen and chlorine are expressed by the figures 1 and 35. Now, every element in the state of gas weighs more than hydrogen, and since any mass of the latter is simply an aggregate of atoms, we say that the atomic weight of hydrogen is 1, *i.e.*, we agree to call its atomic weight unity because its atom is the lightest known.

By this and other methods of research, chemists have arrived at what are called the atomic weights of the elements, these being the ratios by weight, or some sub-multiples thereof, in which these elements respectively combine.

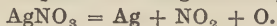
Now the latter statement can only mean that every true chemical compound is definite in composition, *i.e.*, always contains the same elements, united in the same proportion, and this is what we actually find to be the case.

Thus analysis reveals the fact that silver nitrate contains 108 parts by weight of silver, 14 parts by weight of nitrogen, and 48 parts by weight of oxygen, and since 108, 14 and 16 are respectively the atomic weights of silver, nitrogen and oxygen, we must have in the compound in question one atom each of silver and of nitrogen, and three atoms of oxygen.

We therefore write its formula,  $\text{AgNO}_3$ .

Placing some silver nitrate in a hard glass tube, I strongly heat it, and you observe that it at first melts and then begins to give off red fumes.

On continuing to heat it for some time I shall obtain, as a residue, metallic silver only, the red fumes which escape consisting of nitrogen peroxide and oxygen. Since the formula for nitrogen peroxide is  $\text{NO}_2$ , we express the change as an equation, thus—



Mixing in this tube a solution of silver nitrate with one of common salt or sodium chloride, we get a white precipitate of silver chloride, sodium nitrate remaining in solution, a change which, knowing the formulæ of the common salt ( $\text{NaCl}$ ), of the sodium nitrate ( $\text{NaNO}_3$ ), and of the silver chloride ( $\text{AgCl}$ ), we represent by



Since the molecule is made up of a number of atoms, we can, knowing the atomic weights of each of the atoms in it, easily calculate the molecular weight of a compound, and knowing how to express the manner in which that compound reacts with another, we also know the proportions by weight of each compound taking part in the reaction.

Thus in the preceding equation we see that 170 parts by weight of silver nitrate are necessary to yield 143.5 parts by weight of silver chloride, and will yield this quantity of silver chloride when mixed with at least 58.5 parts by weight of common salt.

Since any mass of a substance is merely the aggregate of a large number of molecules, it follows that the ratio by weight in which

the substances concerned react will be true whatever the concrete numbers may be.

Very frequently it is useful to know what is called the equivalent of an element, this being the least weight of that element which unites with one part by weight of hydrogen, and this figure, together with the atomic weights, symbols, and names of the chief elements, is given in the accompanying table:—

### THE ELEMENTS:

THEIR SYMBOLS, ATOMIC WEIGHTS, AND EQUIVALENTS.

	Sym- bol.	Atomic Weight.	Equiva- lent.		Sym- bol.	Atomic Weight.	Equiva- lent.
Aluminium ...	Al	27.02	9.007	Mercury .....	Hg	199.8	99.9
Antimony .....	Sb	120.	40.	Molybdenum.	Mo	95.8	19.16
Arsenic .....	As	74.9	24.97	Nickel .....	Ni	58.6	29.3
Barium .....	Ba	136.8	68.4	Niobium .....	Nb	94.	31.33
Beryllium .....	Be	9.08	4.54	Nitrogen .....	N	14.01	4.67
Bismuth .....	Bi	208.	69.33	Osmium .....	Os	193.	24.125
Boron .....	B	10.9	3.66	Oxygen .....	O	15.96	7.98
Bromine .....	Br	79.75	79.75	Palladium .....	Pd	106.2	26.55
Cadmium .....	Cd	112.	56.	Phosphorus...	P	30.96	10.32
Cæsium .....	Cs	133.	132.7	Platinum .....	Pt	194.3	48.575
Calcium .....	Ca	39.9	19.95	Potassium .....	K	39.04	39.04
Carbon .....	C	11.97	2.99	Rhodium .....	Rh	104.	26.
Cerium .....	Ce	139.9	46.6	Rubidium .....	Rb	85.2	85.2
Chlorine .....	Cl	35.37	35.37	Ruthenium .....	Ru	104.4	26.1
Chromium .....	Cr	52.4	26.2	Selenium .....	Se	78.8	39.4
Cobalt .....	Co	59.	29.5	Silicon .....	Si	28.3	7.
Copper .....	Cu	63.2	31.6	Silver .....	Ag	107.66	107.66
Didymium .....	Di	143.0	47.8	Sodium .....	Na	23.	23.
Erbium .....	E	165.9	55.3	Strontium .....	Sr	87.3	43.65
Fluorine .....	F	19.1	19.1	Sulphur .....	S	31.98	15.99
Gallium .....	Ga	69.	23.	Tantalum .....	Ta	152.	60.67
Gold .....	Au	197.	65.66	Tellurium .....	Te	125.	62.5
Hydrogen .....	H	1.	1.	Thallium .....	Tl	203.64	203.64
Indium .....	In	113.4	37.8	Thorium .....	Th	231.87	57.97
Iodine .....	I	126.53	126.53	Tin .....	Sn	117.8	58.9
Iridium .....	Ir	192.5	48.125	Titanium .....	Ti	48.0	12.
Iron .....	Fe	55.9	27.95	Tungsten .....	W	183.6	30.6
Lanthanum .....	La	138.5	46.17	Uranium .....	U	240.	60.
Lead .....	Pb	206.4	103.2	Vanadium .....	V	51.2	17.07
Lithium .....	Li	7.01	7.01	Yttrium .....	Y	89.6	29.87
Magnesium .....	Mg	24.	12.	Zinc .....	Zn	65.2	32.6
Manganese .....	Mn	55.	27.5	Zirconium .....	Zr	90.	45.

### SUMMARY.

*Matter* is whatever can be weighed, and is made up of *molecules*.

The *molecules* of all bodies are in a state of *motion*.

The *hotter* the body the *more rapidly* the *molecules* *vibrate*.

The *rise in temperature* of a body is usually accompanied by its *expansion*.

*Molecular vibrations* are taken up by the *ether*, and rendered manifest to the *senses*, as *heat*, *light*, or both.

Conversely, the vibrations of the ether should be capable of affecting the molecules, as we shall subsequently learn is the case.

The physical state of a body, *i.e.*, its effect upon light or its temperature, is the result of the distance of its molecules from each other, and of the rate at which they vibrate.

The same body, since it contains a large number of molecules, may exist in different physical states.

In elements, the molecules contain similar atoms, in compounds dissimilar atoms.

The atom is the smallest particle of matter which we can conceive to exist, since it is the smallest particle which can enter into, or leave, a chemical compound.

An element is denoted by a symbol, a compound by a formula.

The density of an element expresses the ratio between the weight of a unit volume of it and a unit volume of hydrogen.

Hydrogen is the lightest form of matter.

The atomic weights of two or more elements express the ratios, or some submultiples thereof, in which they combine.

The equivalents of two or more elements express the simplest ratios in which they combine.

## LECTURE XIV.

DIRECT SYNTHESIS OF SILVER-CHLORIDE—VIBRATORY MOTION OF MOLECULES AND OF THEIR CONSTITUENT ATOMS—EXPLANATION OF CHEMICAL CHANGES BROUGHT ABOUT BY ELECTRICITY OR HEAT—EFFECT OF HIGH TEMPERATURE IN PROMOTING CHEMICAL DECOMPOSITION—ALLOTROPISM AND THE MANNER IN WHICH HEAT BRINGS IT ABOUT—ABSORPTION OF HEAT BY COMPOUNDS WHEN BECOMING CONVERTED INTO THEIR ALLOTROPES—REASON OF THE VARIATION IN STABILITY OF ALLOTROPIC MODIFICATIONS OF THE SAME COMPOUND.

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I HAVE here a jar of greenish-yellow chlorine, and dropping into it some powdered silver you perceive that heat is liberated, and that the silver becomes converted in a white powder. The two elements have, in fact, combined, and I have brought about the direct synthesis of the compound, in accordance with the equation  $\text{Ag} + \text{Cl} = \text{AgCl}$ .

This silver-chloride is a compound extensively used in photography, and taking it as a type we will endeavour to obtain a clear insight into its intimate structure. We have already learnt that the smallest particle of which we can form an idea is the atom, and since this silver chloride is a compound its molecule must contain at least two atoms.

Is there any reason, however, for supposing that in the compound we have merely an aggregate of molecules, each consisting of two atoms? If the substance was a gas the answer to this question would be in the affirmative, but in a solid or liquid there is good reason for believing that what we call a molecule is in reality a structure of considerable complexity containing a very large number of atoms. Whatever be the actual number of atoms in the particular molecule in question, of this we are certain, that not only is each molecule and its constituent atoms in a state of vibration, but that the atoms of each molecule are perpetually changing places with those of the next one.

To illustrate this point I will make use of an electrical experiment. In my lantern is a small glass vessel containing acidulated water, and dipping in it are two platinum electrodes. Projecting its image on the screen I pass a current of electricity generated by a single Grove's cell through the liquid, and as no bubbles of gas are perceived clinging to the platinum electrodes we conclude that no decomposition has taken place. Now, using two Grove's cells, the bubbles of gas which make their appearance at the two platinum electrodes teach us that with this current we have succeeded in decomposing the water.

What explanation does science give of this phenomenon? Simply this, that before we passed the current at all the atoms of hydrogen and oxygen, constituting by their union the compound water, were exchanging partners in all directions at the same time, but the instant a current was passed of sufficient energy to decompose the compound then the atoms became so influenced that certain of them, viz., the hydrogen atoms, in the immediate vicinity of one pole or electrode travelled in one direction only, the oxygen atoms in the vicinity of the other pole travelling in the opposite direction, and certain atoms being thus prevented from re-uniting with other atoms of different nature united with each other, and gave by their union the oxygen and hydrogen gases appearing at each pole.

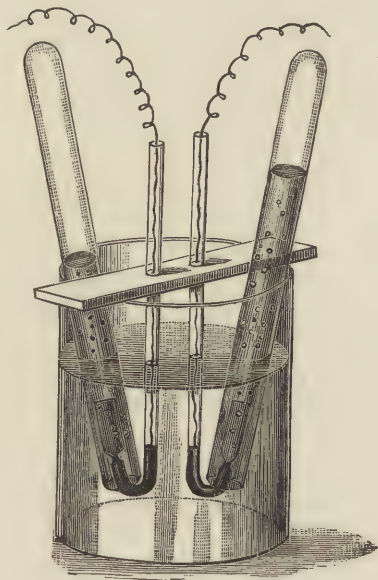


FIG. 51.—DECOMPOSITION OF WATER BY AN ELECTRIC CURRENT.

This explanation is borne out by the fact that to decompose the water we require a certain minimum current, its energy being a measure of the energy with which the dissimilar atoms tend to recombine.



Reverting to our silver chloride, we must learn, therefore, to look upon the atoms in each molecule of it as in constant motion, the molecule itself being not in a state of statical equilibrium, in which two forces exactly balance each other, but in a state of dynamical equilibrium, due to the fact that two similar reactions are continually taking place in opposite directions. Representing two molecules by  $\text{AgCl}$  and  $\text{Ag}^1\text{Cl}^1$ , we have at one instant  $\text{AgCl}$ ,  $\text{Ag}^1\text{Cl}^1$  and at another  $\text{AgCl}^1$ ,  $\text{Ag}^1\text{Cl}$ , and because of these atomic motions each atom possesses a certain amount of kinetic energy and has a certain momentum, the motion serving, in fact, to equalise the distribution of the energy and of the momentum. Chemical equilibrium means, viewed in this light, that the velocity with which  $\text{Ag}$  moves towards  $\text{Cl}^1$  is the same as that with which  $\text{Ag}^1$  moves towards  $\text{Cl}$ , and if we altered these velocities then the compound would be decomposed.

We might bring about this difference in velocity, just as we did in the case of water, by passing a certain minimum current through the compound; but, as we shall see in a moment, there are many other ways of obtaining the same result.

If, for instance, we heat such a compound, what is it that we actually do? Silver exists as such, and so does chlorine, *i.e.*, we can have molecules consisting only of atoms of silver or of atoms of chlorine. No rise in temperature will produce from silver anything but silver or from chlorine anything but chlorine, because what we might call  $\text{AgAg}^1$ ,  $\text{ClCl}^1$  is the most stable system possible.

But by heating the compound silver chloride we evidently give greater freedom of motion to the atoms  $\text{AgAg}^1$  and  $\text{ClCl}^1$ , and so lessen the chances of recombination between  $\text{AgCl}$  and  $\text{Ag}^1\text{Cl}^1$ , or what amounts to the same thing, we increase the chances of recombination between  $\text{AgAg}^1$  and  $\text{ClCl}^1$ .

By gradually raising the temperature of the compound, we will, in fact, finally reach a point at which the atom  $\text{Ag}$ , having left  $\text{Cl}$ , no longer recombines with it, but with  $\text{Ag}^1$ , and the atom  $\text{Cl}^1$  then combining with  $\text{Cl}$ , we have the far more stable result  $\text{AgAg}^1$ ,  $\text{ClCl}^1$ . When this point is reached we say that the temperature has been sufficient to effect the decomposition of the compound. Supposing, however, we raise the temperature of the silver chloride to a degree insufficient to decompose it, the compound must, under these conditions, be less stable than it was when colder, for the reasons just pointed out.

Pouring some water over the silver chloride contained in this test tube, I raise the mixture to the boiling point, and you perceive that no blackening occurs, showing that a rise in temperature of  $100^\circ\text{C}$ . is insufficient to decompose silver chloride.

Now, decanting off the water, I pour over the silver chloride a cold mixture of grape sugar and caustic potash, and you again see that no decomposition has taken place; but if I heat the mixture, then blackening occurs, this being the result of the actual decomposition of the silver chloride.

When the mixture was cold the chances of Ag recombining with  $\text{Cl}^1$  were greater than its chances of recombining with  $\text{Ag}^1$ , but on heating it these chances were so decreased that the silver atoms combined with each other, and the compound was decomposed. We see from this that if we supply a compound with an amount of energy, say as heat, insufficient to cause decomposition, the energy so supplied may facilitate the decomposition of that compound by another one.

In the case in point the mixture of grape sugar and caustic potash tended to become indirectly oxidised at the expense of the chlorine of the silver chloride, and, when we raised the temperature sufficiently, did actually become oxidised, although the comparatively slight rise in temperature was quite insufficient of itself to decompose the silver chloride.

It is evident that, in this case, the change of state due to increased temperature was only a transient one, for if it was permanent, or lasted, at all events, for even a short time, the silver chloride which had been heated, and then cooled, would have been decomposed by the grape sugar, just as well as if they had been placed in contact with each other at the higher temperature.

Is there any reason for believing that a rise in temperature, or some other source of energy, can without decomposition produce a relatively permanent change of state?

To answer this question I take some of this red mercuric iodide, and smear it with a tuft of cotton wool over a piece of paper. Now gently heating the mixture over the Bunsen burner, you see that the red colour has changed to yellow.

What is the cause of this? The compound has not been decomposed, *i.e.*, it still contains the same elements united in the same proportion, but if we took the trouble to place the original red solid, and this its yellow modification, under a powerful microscope, we should see that the red solid consisted of octahedral crystals, and the yellow of rhombic tables, the different colours being purely the result of the different action of the crystals upon white light.

Tracing a design with the tip of this feather upon the yellow powder, you see that the design comes out red on a yellow ground, a very slight force being sufficient to cause the rhombic crystals to revert to their original octahedral condition. In this crucible I have a quantity of these yellow crystals, which have been prepared by carefully heating red mercuric iodide, and in the centre of the whole is placed a thermometer, which at the present moment indicates a temperature of  $12^{\circ}\text{C}$ . Stirring up the crystals with the thermometer, I at once re-convert them into their original condition, and looking at the thermometer, I perceive that it has risen to  $15^{\circ}\text{C}$ .

Just, in fact, as by heating the substance it must have absorbed an amount of heat sufficient to change it into its allotropic modification, so precisely the same amount of heat is given out

when that allotropic modification reverts to its original and more stable form.

If I raise the original red solid to a high temperature, then it is decomposed, but you will concede that the amount of heat required to do this must be far greater than that required to convert it into its allotropic form, and not only is this the case, but by actual decomposition we convert the compound not into a less stable substance, but into two more stable substances, viz., its constituent elements.

Now the amount of heat or any other form of energy necessary to decompose a given quantity of any compound admits of ready calculation, for we can measure the quantity of heat liberated when its two elements combine, and this measures the energy necessary to decompose it.

Supposing we did this with mercuric iodide, and found the amount of heat liberated when its elements combine to form two grains of the substance to be, say, 100 units. If now, having got the two grains of the compound, we found that an amount of energy equal to only one unit brought about a distinct change in its properties, the inference that the change so brought about was due to direct decomposition would surely be untenable.

But knowing that an amount of energy, much smaller than that necessary to produce undoubted decomposition, would suffice to convert the mercuric iodide into its allotrope, we ought to very reasonably conclude that this was the kind of change which had actually occurred.

Let us assume for the moment that we have a number of relatively stable molecules of silver chloride one over the other, and that we have by some means converted the top one into a less stable allotropic modification of the same substance.

Then this molecule, being less stable than before, should admit of more ready decomposition. If now we bring in contact with the substance a developer having no action upon unchanged silver chloride, it may, nevertheless, act upon the molecule of allotropic silver chloride.

More than this, since heat (say) was absorbed in converting the stable into the unstable silver chloride, this heat will be liberated when the unstable compound is converted into a more stable form, and the actual amount of decomposition being really due to the interaction of the two substances aided by this liberated heat may be greater than what the actual amount of heat (or energy) absorbed would lead us to suppose.

Calling  $H$  the number of heat units liberated when the chlorine and silver combined to form their most stable compound, and  $H^1$  the number of units absorbed when this compound becomes converted into a less stable allotrope, then  $H - H^1$  will measure the number of heat units liberated when that allotrope is decomposed into chlorine and metallic silver. This amount of energy superadded to the chemical energy of the developer may

cause a series of other unchanged molecules beneath the first to be attacked, but as, of course, we have only a measurable quantity  $H-H^1$  of heat, the number of unchanged molecules decomposed will, although greater than unity, be, relatively speaking, very small, the greater part of the liberated heat being here spent, not in effecting decomposition, but in warming up the developer.

It is far otherwise, however, if we take a solid body whose molecules in a state of unstable equilibrium are capable of being decomposed by a slight blow.

Then, on disturbing that equilibrium at any point, the heat liberated at that point may be sufficient to decompose the portion of the compound in the immediate vicinity, and the action spreading in this way from one portion of the compound to another may, in the long run, result in decomposing every portion of it.

Touching, for instance, this iodide of nitrogen with a feather, it decomposes with a loud explosion, the amount of energy liberated as heat being here out of all proportion greater than the energy of the blow which originated the decomposition.

#### SUMMARY.

*Chlorine gas combines directly with metallic silver, the act of combination being accompanied by a rise in temperature.*

*The molecules of most gases contain two atoms, but the molecules of solids and liquids are much more complex structures.*

*In a compound, the constituent atoms are perpetually changing partners.*

*Passing a current of electricity through certain compounds is said to decompose them, the real cause of the decomposition being the influence which each electrode exerts upon the atoms. Certain atoms are attracted towards an electrode at a high potential, others towards the other electrode at a lower potential.*

*In an element the atoms are in more stable equilibrium than in a compound.*

*By heating a compound, we give greater freedom of motion to the atoms, and so decrease their chances of combining with other dissimilar atoms.*

*When the temperature reaches the point at which the compound decomposes, then similar atoms combine with each other, forming a more stable system.*

*If the temperature is insufficient to cause decomposition, we enhance the facility with which decomposition may be brought about by some other cause.*

*A rise in temperature may bring about a change in the arrangement of the atoms in the molecules without producing decomposition. This allotropic form of the original compound must be less stable than the original.*

*During the reversion of the allotrope of a compound into its original and more stable state, heat is liberated, and the consequent rise in temperature may facilitate the decomposition when once started.*



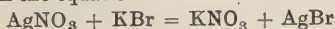
## LECTURE XV.

METATHESIS OF SILVER HALOIDS—ACTION OF LIGHT UPON THEM PRODUCING VISIBLE DECOMPOSITION—LIBERATION OF THE HALOGEN DURING EXPOSURE—THE OXYSALT, SUBSALT, AND PHOTOSALT THEORIES OF THE VISIBLE IMAGE—RESEARCHES OF TOMMASI, HITCHCOCK, AND CAREY LEA—EFFECT OF EXTREMELY PROLONGED EXPOSURE—REASON OF LESSER DEGREE OF DARKENING OF SILVER IODIDE AS COMPARED WITH SILVER CHLORIDE.

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SILVER bromide, being the chief substance employed in negative making, it will be convenient to begin our study of silver compounds with it.

Pouring into the cold solution of silver nitrate contained in this tube a cold solution of potassium bromide, a slightly yellow flaky precipitate of silver bromide falls to the bottom, produced in accordance with the equation



a species of chemical change which we designate as metathesis or chemical substitution.

This silver bromide gives, as you doubtless remember, a developable image when exposed for a short time to actinic light, but on prolonging the exposure to what is relatively an enormous length of time, we get, instead of a developable image, a comparatively faint printed-out one.

It will be convenient to begin with the study of the latter image first.

The visible darkening produced in this case can be proved in the most conclusive manner to be due to the liberation of bromine by the silver bromide.

I will endeavour to satisfy you upon this point in the following way. Here I have paper impregnated with a mixture of starch and potassium iodide, and, causing the bromine vapour liberated from the liquid bromine contained in this bottle to act upon it for a moment, you see that the colourless paper changes to an intense blue, the change of colour being due to the interaction between the starch and the iodine set free by the bromine from the potassium iodide. It is true that many other substances, such as hydrogen-peroxide, ozone, and nitrous fumes will bring about a similar result, but if I produce the result under conditions which I know to be unfavourable to the production of these substances, the inference would clearly be that the change is due to free bromine. In this tube I have some moist silver bromide, and suspended im-



mediately over it is a strip of the test paper. Burning about a yard of magnesium wire in front of the tube, you perceive that the paper is blueed, and, as under these conditions none of the other substances which change its colour could have been produced, the inference is that the light emitted by the burning magnesium caused the silver bromide to liberate bromine.

Indirectly I can prove the same thing in this way. Making a cross with a solution of sodium sulphite on a piece of paper impregnated with silver bromide, I burn some magnesium in front of the paper, and you perceive that it has darkened most where sodium sulphite was present.

Now, placing this jar of bromine vapour over this dish containing a strong solution of sodium sulphite, you see the bromine vapour is rapidly absorbed. Sodium sulphite is then a bromine absorbent, and it facilitated the visible darkening precisely because, by absorbing the bromine, it facilitated the separation of the latter from the silver.

If, on the other hand, I mark on the paper a cross with a solution of bromine, and then expose the whole to the light of the burning magnesium, you see that the darkening is least wherever bromine is present, the reason being that bromine has little or no tendency to combine with itself.

It might be thought from this that the removal of the bromine was essential to the occurrence of the reaction, but reasoning by analogy, from what has been observed with silver chloride we should be inclined to say that this would not be the case. It has been found, for instance, that perfectly pure and dry silver chloride changes colour in a vacuum, but becomes reconverted into its original state in the dark,\* and a similar result would in all probability be found to hold good with silver bromide. With silver iodide, however, the case is probably different, the presence of an iodine absorbent being essential to its darkening, and the reason of this will be apparent later on.

Since, then, it is conceded that the visible change is due to the liberation of bromine, the next question is, what is the precise nature of that change?

Since silver bromide is represented by the formula  $\text{AgBr}$ , it might at first sight appear that the equation  $\text{AgBr} = \text{Ag} + \text{Br}$  would give expression to what actually occurs. And it appears highly probable that if the action of light is sufficiently prolonged, and means are taken to expose every portion of the substance to its action, this actually represents the change.†

Usually, however, we get, on exposing silver bromide to light for a considerable time, a product which is not wholly soluble in nitric acid, and which cannot, therefore, consist of metallic silver only.

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\* Tommasi, "Annal. Phys. Chemie," 1879, p. 621.

† R. Hitchcock, *B. J. Phot.*, 1890, p. 9.

Here, for instance, I have in a tube some silver bromide which has been exposed to light for a week, the change being facilitated by placing over the silver bromide a strong solution of sodium sulphite.

Now, pouring strong nitric acid over the product, you see that it is practically unaffected, whilst the same nitric acid poured over the metallic silver in powder contained in this other tube at once dissolves it.

What, then, is the nature of this product which nitric acid does not attack? It appears highly probable that this substance, which varies in colour and in properties according to the length of time during which the silver bromide has been exposed to light, is a compound containing less bromine than silver bromide.

According to some observers, it is a sub-bromide, the change being represented by  $2\text{AgBr} = \text{Ag}_2\text{Br} + \text{Br}$ , but this is hardly in agreement with well-known chemical facts, for silver sub-bromide should, according to all analogies, be exceedingly unstable, and the reverse is actually the case. But if we assume that the darkened product is a compound formed, perhaps, by the union of silver sub-bromide and silver bromide,\* then such a compound should be, and actually is, a relatively stable one.

I can illustrate this point in the following way:—In one of these tubes I have copper sulphate in its usual condition, in which a molecule of it is combined with five molecules of water, and in the other tube the same salt deprived of this water. Now, placing the two tubes side by side over this Bunsen burner, we soon reach a point at which the dehydrated copper sulphate is decomposed, as is evidenced by the acid fumes it emits. At that instant of time the ordinary copper sulphate is still, as you see, undecomposed, and only decomposes when the flame is permitted to act upon it for a longer period. This is, of course, just what we might expect, for to dehydrate the anhydrous and easily decomposed copper sulphate I had to expend a certain amount of energy upon it, and the same amount has to be spent upon the hydrated salt *before* decomposition could begin.

For chemical reasons, the simplest formula we could assign to a compound of silver sub-bromide and silver bromide would be  $\text{Ag}_5\text{Br}_3$ , and this is the formula we shall provisionally adopt, calling this substance silver photo-bromide for want of a better name.

It has been stated that silver bromide, chloride or iodide form oxybromide, oxychloride or oxyiodide on exposure to light. This seems extremely improbable, as it has been shown† that pure and dry silver chloride darkens in a vacuum or in substances containing no oxygen,‡ and again|| that the loss in weight ex-

\* Carey Lea, *B. J. Phot.*, 1887, p. 345.

† Tommasi, *loc. cit.*

‡ Carey Lea, *American Journal of Science*, Vol. III., p. 38.

|| R. Hitchcock, *loc. cit.*

perienced by silver chloride exposed to light under conditions favourable to the production of oxychloride is greater than the quantity of chlorine collected, whilst it should have been the same had the oxychloride theory been true.

Summing up so far we may say that the dark product formed when silver bromide is exposed to light consists of varying quantities of silver photo-bromide mixed with unaltered silver bromide, the quantity of photo-bromide increasing *pari passu* with the intensity and duration of the light, bromine being simultaneously liberated. When a certain quantity of silver bromide has been converted into photo salt, then the further action of light probably begins to decompose the photo-bromide first formed into bromine and metallic silver, and if the particles of silver bromide are sufficiently minute to permit the light to very completely act upon them we may finally effect the complete decomposition of the photo-bromide into silver and free bromine.

Evidently it may and does happen that the layers of photo-bromide first formed are actually decomposed before the whole of the silver bromide has been converted into photo salt, and this is the reason that nitric acid will dissolve out from the same sample of silver bromide exposed to light for varying periods different amounts of metallic silver.

Taking, for instance, a comparatively thick film of silver bromide which has been exposed to light at the top only we have in it (a) free metallic silver, (b) silver photo-bromide and unaltered silver bromide, the relative quantities of which will depend upon the length of time during which light has acted.

What is true of silver bromide is also probably true of silver chloride and iodide, *i.e.*, that on exposure to light these substances become converted into photo salts (the latter, however, only on condition that an iodine absorbent is present), liberating in so doing free chlorine or free iodine.

I now show you three tubes containing silver chloride, bromide, and iodide, prepared by similar methods and exposed for corresponding periods to light under water. You will observe that the chloride has darkened most, and the iodide least, the silver bromide darkening to an intermediate degree. From purely chemical reasons we should have expected the reverse of this, for the silver iodide is the certainly least stable compound.

In fact, the stability of the three compounds, measured by the method sketched in the last chapter, is roughly as 3, 2, 1, the chloride being three times as stable as the iodide.

But we must remember that the darkening is due to two things: Firstly, to the production of photosalt, and, secondly, to the conversion of a portion of this into metallic silver.

Now, it has been shown by Carey Lea\* that silver photochloride,

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\* B. J., 1887, p. 346.

bromide, and iodide are for the most part indistinguishable from each other so far as colour is concerned, and we must, therefore, look upon the greater darkening of the silver chloride as due to the production of a greater quantity of silver photochloride or of a greater quantity of metallic silver. It would appear, however, that a longer exposure to light should suffice to darken the iodide to the same depth as the chloride, but, as a matter of fact, such is not the case, no amount of exposure sufficing to cause the silver iodide to assume a colour of the same depth as that assumed by the silver chloride. How do we explain this result? Precipitating some silver iodide by mixing solutions of silver nitrate and potassium iodide, I shake up the precipitate with some of the yellow solution obtained by dissolving potassium iodide and iodine in water, and you see that it is at once decolourised. To prove the fact that no free iodine is present in the supernatant liquid, I add it to a solution of starch, and you perceive that no blue colouration is produced. Now, making silver chloride in a similar manner, I shake up chlorine water with it, and add the supernatant liquid to a mixture of starch and potassium iodide, when the blue colour, due to the liberated iodine acting upon the starch, tells us that no chlorine has been absorbed.

Silver chloride does not, in fact, combine with chlorine, but silver iodide does combine with iodine.

Now we have learnt that, if the silver chloride or iodide are to be converted into photosalt, they must part with chlorine or iodine, and we now see that, so far as the former is concerned, chlorine does not combine with silver chloride, whilst iodine does combine with silver iodide.

We can, therefore, readily understand that the amount of photoiodide which we can form by exposing silver iodide to light is limited, owing to the fact that the iodine absorbed by the silver iodide will prevent its further change.

In the case of our tube of partially darkened silver iodide, for instance, light acting upon the surface of each particle of substance liberates iodine. A portion of this dissolves in the water, and probably reacts upon it; the other portion combines with the subjacent iodide and prevents further action.

In the case of the chloride we have a different state of affairs. Here the liberated chlorine does not combine with the subjacent layer of silver chloride, and so the change can more readily take place.

Silver bromide occupies an intermediate position, bromine tending to combine with it to a lesser extent than iodine tends to combine with silver iodide, but to a greater extent than chlorine tends to combine with silver chloride, and so the darkening, which measures, you remember, the amount of photosalt formed, is greater with the iodide but lesser than with the chloride.



## SUMMARY.

*Metathesis is the double exchange of elements occurring when certain compounds are brought together.*

*Chlorine, bromine and iodine are called the halogens; silver chloride, bromide or iodide are called haloid salts.*

*A silver haloid liberates its halogen when exposed to actinic light for a sufficiently long period.*

*The darkening of a silver haloid is accompanied by the liberation of the halogen.*

*Any haloid absorbent will facilitate the darkening of a silver haloid.*

*Free iodine colours starch blue.*

*Free bromine or chlorine liberates iodine from a haloid.*

*The silver haloids darken in vacuo and in absence of oxygen.*

*Very prolonged exposure to light decomposes certain silver haloids into silver and the halogen.*

*Comparatively short exposure to light decomposes all the silver haloids into silver photo-salts.*

*A silver photo-salt is much more stable than a sub-salt.*

*Silver chloride does not combine with chlorine, but silver iodide combines with iodine.*

*Prolonged exposure to light darkens silver chloride very considerably; no exposure to light darkens silver iodide to the same degree.*



## LECTURE XVI.

INVISIBLE CHANGE PRODUCED BY LIGHT UPON SILVER BROMIDE—  
ALLOTROPIC MODIFICATIONS OF THIS SUBSTANCE—ACTION OF HEAT  
UPON INSENSITIVE SILVER BROMIDE—ANALOGY BETWEEN ITS  
ACTION AND THAT OF LIGHT—THE CHEMICAL THEORY OF THE  
DEVELOPABLE IMAGE AND ITS SO-CALLED PROOFS—A SUGGESTED  
THEORY OF THE EFFECT OF LIGHT UPON THE SILVER HALOIDS.

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YOU are all, of course, familiar with the fact that an exceedingly short exposure to light will so change silver bromide as to enable a developer to act upon it, although the change may be invisible to the unaided eye before the developer was applied.

That light has produced a change must be conceded, and we must now consider what the precise nature of that change is.

Taking silver bromide as a type, this substance is well known to exist in a variety of allotropic forms, chemically the same, so far as the quantities of silver and bromine which they contain are concerned, but different, nevertheless, in colour, appearance, and in the effect upon them of what we call a developer.

Of the existence of the same element or compound in various allotropic forms we have many excellent examples.

Here, for instance, is yellow, intensely poisonous, inflammable phosphorus, and beside it is a red, non-poisonous, and comparatively unflammable substance, which, although it differs so much from what we are in the habit of calling phosphorus, is, nevertheless, the same element.

Here, again, I have an almost white powder, a yellow solid, and a plastic indiarubber-like mass—all allotropes of the same element, sulphur. The element carbon affords us a third example of allotropism, existing as it does in the crystalline transparent form (diamond), as opaque black crystals (graphite), as a soft black powder (lampblack), or as a hard, brownish-black solid (gas coke).

Compounds, as well as elements, exist in allotropic forms. I have already shown you that this is the case with mercuric iodide, but there are many other examples.

Here, for instance, is a piece of opaque white marble, and beside it is a transparent crystal of calc spar and some precipitated chalk. No one, to look at these three things, would imagine that they contained the same elements—combined in the same proportions—

but such, nevertheless, is the case, all three being calcium carbonate.

Here, again, I have a white powder, a translucent semi-crystalline substance, and a transparent crystal—all allotropic modifications of calcium sulphate.

Silver bromide exists in the several allotropic forms tabulated below:—

#### ALLOTROPIC MODIFICATIONS OF SILVER BROMIDE.

No.	Colour by transmitted light.	Colour by reflected light.	Photographic occurrence.	Action of alkaline developer upon the substance without previous exposure to light.
1	Orange.	Slaty blue.	Very fresh collodion emulsions.	No effect.
2	Ditto.	Bluish white.	Ripened collodion emulsions and wet collodion.	Ditto.
3	Reddish.	Ditto.	Very sensitive wet collodion.	Ditto.
4	Ditto.	Yellowish white	Very old collodion emulsions.	Ditto.
5	Violet blue.	Ditto.	Ditto.	Slight action after long contact.
6	Ditto.	Greenish yellow.	Very fresh gelatine emulsions.	Greater action than upon No. 5.
7	Ditto.	Green.	Ripened gelatine emulsions.	Greater action than upon No. 6.
8	Blue.	Indistinct.	Very old gelatine emulsions.	Immediate blackening.

I will begin by showing you how these allotropes of silver bromide are prepared.

Placing in this tube a rather dilute and cold solution of potassium bromide, I add to it one of silver nitrate, when you see that an almost white precipitate falls.

This is our second allotrope, and by shaking it up vigorously or by gently heating it, I convert it into the third allotrope, which, although still nearly white by reflected light, is seen by transmitted light to be distinctly redder than before.

Employing now concentrated solutions of potassium bromide and of silver nitrate I obtain the fourth allotrope, which again by vigorous agitation, or by gentle heat, I convert into the next or fifth variety, into which, in fact, all the previous varieties would in time become converted on gently heating them.

I now alter the conditions of the experiment by mixing the silver nitrate with this solution of gelatine and potassium bromide, when a precipitate falls identical in composition with that just obtained in a different way, and by gently heating the viscous liquid I change that precipitate into the sixth, seventh and eighth allotropes respectively, the change being accompanied by a very visible alteration in the colour of the substances by reflected light.

We learn, therefore, that energy applied as heat will gradually convert any of these allotropes into what we may call the eighth variety.

We must now study their behaviour towards an alkaline developer.

Causing my attendant to turn on the red light, I mix in a test tube some silver nitrate with a cold solution of potassium bromide and gelatine, and pour half of the emulsion, as the result is called, on a glass plate.

Now placing the tube in this bath of hot mercury heated from below by a Bunsen burner, which is itself invisible, I cause the mixture to enter into ebullition, and keep it so for five minutes. By so doing I produce, you remember, the eighth allotrope. Now pouring some of this upon a glass plate, I put it, when the emulsion has set, side by side with that on which I had previously placed the fifth allotrope, into this dish containing a rather strong alkaline solution of hydroquinone, and on removing the plates you see that the eighth allotrope is blackened all over, whilst the fifth allotrope has remained unchanged.

The blue modification of silver bromide fogs, therefore, without exposure to light at all, and its production from the fifth allotrope is brought about by a rise in temperature.

Whilst I have been carrying on these experiments my assistant has been immersing one end of a slip of thin glass coated with ordinary commercial emulsion into the hot mercury bath, and he has marked with a pin scratch the end immersed in the mercury.

Placing this slip of glass in the developer for a few minutes and then removing it, you perceive that it has fogged where immersed, the rise in temperature having, in fact, enabled the developer to fog the solid mass of emulsion just as truly as it enabled the developer to fog the same emulsion when heated whilst liquid.

Now if we exposed the other half of the slip of glass first used to actinic light and then immersed it in the developer, you are aware of course that half would fog also.

We might, in fact, take a plate, expose half of it to light, and heat the other half without previous exposure to light, when we should find that the developer would act in an identical way upon both portions.

It appears, therefore, very reasonable to suppose that the action of light is similar to that of heat, viz., it converts the allotrope of silver bromide used into that allotrope which fogs on the application of a developer.

Many authorities hold, however, the view that the action of light in producing a developable image differs in degree only, and not in kind, from its action when producing a visible image, and we must clearly bear in mind that these authorities hold that even an exceedingly short exposure to light, say such an exposure as one-tenth of a second at a yard from a candle flame, produces the same result as an hour's exposure to brilliant sunshine, the only difference

according to them being that in the latter case the number of molecules altered is very much greater than the former.

Now the amount of energy as heat or light requisite to decompose a single molecule of silver bromide into silver and bromine can be calculated if we know the weight of that molecule and the number of units of energy necessary to decompose a given weight of the substance.

Fortunately, both data are available. Taking the specific gravity of silver bromide as six, it may be shown from Sir Wm. Thompson's research on the size of molecules\* that in a piece of it of the size of this small cube of wood (a cubic centimetre) there are at least  $3 \times 10^{24}$  molecules, and from this it at once follows

that each molecule weighs  $\frac{6}{3 \times 10^{24}}$  grammes (a gramme equalling practically 15 grains).

Now when one gramme of silver combines with one gramme of bromine, energy equivalent to 211 heat units is developed;† therefore, to decompose two grammes of silver bromide, we should require an amount of energy equal to 211 heat units, or to

decompose a molecule of it we should want  $\frac{6 \times 211}{3 \times 2 \times 10^{24}} = \frac{211}{10^{24}}$

heat units. It is assumed, however, by those who hold the views we are now discussing that some of the necessary energy is supplied by the union of the bromine with the gelatine. Let us grant that this is the case, and assume that in consequence the actual amount of energy requisite to convert a molecule of silver bromide in gelatine into silver sub-bromide is one hundred times

less than we have supposed, or  $\frac{211}{10^{26}}$  heat units.

Now, by exposing a sensitive plate for  $\frac{1}{10}$ th of a second to the light given out by a standard candle, a metre (39·37 inches) from it, we can produce a decided fogging.

What amount of energy is supplied by a candle in that time? It can be shown‡ that such a candle produces at its source 2·19 units of heat in  $\frac{1}{10}$ th second, but of this only about 15 per cent. is utilised, and of the remainder only about five per cent. is capable of affecting the sensitive plate as light, so that at the source, so far as the plate is concerned, we have an amount of energy equivalent to only ·0219 units, or, in round numbers,  $\frac{1}{50}$ th of a heat unit.

Assuming, now, that the distance from centre of candle to margin of flame is one centimetre, at a metre distance the energy would only be  $\frac{1}{10,000}$  of this, or  $\frac{1}{500,000}$  heat units. We have

\* *Nature*, Vol. I., p. 551 *et ante*.

† Hurter and Driffield, *Photography*, Vol. III., p. 136.

‡ Hurter and Driffield, *loc. cit.*



seen that to decompose a molecule of silver bromide into sub-bromide and bromine, energy equivalent to  $\frac{211}{10^{26}}$  heat units are required, consequently the amount of energy given out in  $\frac{1}{10}$ th second by the burning candle would suffice to decompose, in round numbers,  $10^{17}$  molecules  $\left(\frac{1}{500,000} \div \frac{211}{10^{26}}\right)$ .

Now if, instead of having taken a flat plate, we had taken a spherical one of a metre (39·37 inches) radius over the whole of that surface, the silver bromide would have been acted upon so as to fog on the application of a developer. The area of such a surface would be 125,664 square centimetres, or 19,482 square inches, and upon the top layer of this large surface, if the chemical theory is true, there should be  $10^{17}$  molecules. How many are actually present?

Sir Wm. Thompson's research again comes to our aid, for he tells us that the distance from centre to centre of a molecule is

from  $\frac{1}{140,000,000}$  to  $\frac{1}{464,000,000}$  of a centimetre, the smaller of which figures we will adopt.

Now, an area of 125,664 square centimetres is equivalent to a square whose side is  $\sqrt{125,664} = 354$  centimetres nearly, and along this

there should be  $\frac{1}{140,000,000}$  ( $= 4956 \times 10$ ) molecules, and in the entire square,  $24,561,936 \times 10^{14}$  molecules.

This supposes, however, that we are dealing with a surface wholly made up of silver bromide, which is not, of course, the case. In an average gelatino-bromide emulsion we have about half per cent. by volume of silver bromide, so that we must divide the number of molecules just arrived at by 200. Doing this we get as result,  $1,228,097 \times 10^{14}$ , or, in round numbers,  $10^{21}$  molecules.

It is evident, therefore, that the amount of energy actually received by the plate is disproportionate to the amount required to decompose the surface molecules of silver bromide into silver sub-bromide, and bromine even, granting that the energy required to effect this decomposition is one hundred times smaller, owing to the presence of the gelatine, than that required to decompose the silver bromide into silver and bromine.

Again, if a short exposure to light resulted in the liberation of bromine this should admit of detection, but it has been conclusively shown\* that no bromine can be detected, and the inference is, therefore, that none had been liberated.

Or to take another line of argument—if the change was due to chemical decomposition, and to that only, the amount of change

\* Hurter and Driffield, *loc. cit.*



should increase *pari passu* with the amount of energy absorbed. This is indeed the case up to a certain point, but beyond that point the amount of change goes on decreasing.

I will illustrate the fact for you in the following way: In this dark slide I have an ordinary sensitive plate, and drawing out the shutter a little I expose a portion of the plate for ten seconds to the light emitted by magnesium burning two inches in front of it. I now increase the distance to a yard, and drawing out the shutter still more I expose a fresh portion of the plate for ten seconds. Increasing now my distance to 12 feet, and uncovering the entire plate, I give an exposure of one second. On developing the whole we have, as you see, a dense deposit on the portion which has received the shortest exposure, a more dense deposit on the middle, and a less dense deposit on the portion which has received the longest exposure.

We would, in fact, by giving different portions of the same plate a series of gradually increasing exposures get densities which, up to a certain point, increased with the exposures, but beyond that point decreased with them, and the break in the nature of the action would, for well-known scientific reasons, indicate either an alteration in the nature of the change undergone by the plate or a change in the developer. Since it cannot be a change in the latter it is only reasonable to suppose that it is a change in the former.

A simple experiment will enable us to realise the bearing of these results upon the question at issue.

Giving this plate a short exposure to light, I mark a cross on it with bromine water, and then develop the whole, when you see that the cross comes out white on a dark ground. The image then, whatever may be its nature, is destroyed by bromine. Now, we know that a long exposure to light will liberate bromine from silver bromide. What more reasonable, therefore, than to conclude that the partial destruction of the effect, which we have just learnt is the result of enormous over-exposure, is actually due to the action of the bromine liberated by over-exposure upon the material of the film as yet unacted upon in the same way?

Summing up, therefore, we may say—(1) That there is no evidence of the liberation of bromine during a short exposure, although it is undoubtedly liberated if the exposure is sufficiently prolonged. (2) That the amount of energy known to affect the plate during that short exposure is too small in amount to account for the separation of bromine from silver bromide. (3) That the effect of a developer upon a plate exposed to light is identical with its effect upon the same plate when heated in non-actinic light, which latter is conceded to allotropise the silver bromide. It follows from all this that we may look upon the silver bromide in a sensitive plate exposed to light as undergoing a gradual allotropation, this being complete, so far as a single molecule is concerned, when that molecule has been converted into the blue modification of the same substance which fogs without exposure to light on the appli-

cation of a developer, and that a further exposure results in the separation of bromine from that allotropic molecule to form Carey Lea's photobromide.

We are not without examples of the action of light in producing allotropic forms of the same compound.

Here, for instance, I have a massive blood-red solid, and beside it is a fine powder much lighter in colour. This latter was originally a portion of the former solid, and the change has been brought about simply by exposing the solid for six months to the action of light. If, then, light can change blood-red realgar, as the substance is called, into an allotrope, is it not reasonable to suppose that it can, and does, bring about a similar change in silver bromide?

#### SUMMARY.

*Light acts upon silver bromide to produce a change, which, although invisible to the eye, may be rendered visible by development.*

*Heat causes insensitive silver bromide to fog on the application of a developer.*

*The effect of heat upon silver bromide is conceded as resulting in allotropicising it.*

*Many allotropes of silver bromide are known to exist, and of these one is immediately fogged by a developer, even if prepared in non-actinic light.*

*The action of light and heat upon silver bromide are up to a certain point probably similar, i.e., they both convert it into its allotrope most readily acted upon by a developer. Beyond that point they both decompose it.*

*The amount of energy requisite to produce chemical decomposition of silver bromide can be calculated, and that amount is found much too large to support the view that a short exposure will decompose it.*

*The amount of energy required to allotropicise a compound is always much less than the amount required to split it up into its elements.*

*Proof is wanting that a short exposure liberates bromine from silver bromide, although a longer exposure will undoubtedly do so.*

## LECTURE XVII.

PREPARATION OF SILVER NITRATE FROM COIN—ACTION OF HEAT AND OF NITRIC ACID AND OF COMMON SALT UPON SILVER AND COPPER NITRATES—ACTION OF METALLIC COPPER UPON SILVER NITRATE—SEPARATION OF SILVER FROM SILVER CHLORIDE—THE SO-CALLED “NASCENT STATE”—ACTION OF LIGHT UPON A MIXTURE OF HYDROGEN AND CHLORINE—UTILISATION OF OLD FIXING BATHS.

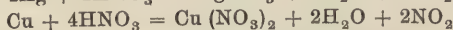
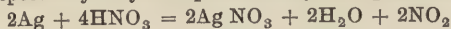
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IT will be convenient at this stage to give some little time to the consideration of the methods employed in preparing the salts of silver used in photography. Beginning with the pure metal itself, of which I hold a piece in my hand, you perceive that it is so soft as to be scratched by the finger nail, and quite useless on that account for coinage or ornamental articles.

To harden silver, it is alloyed with copper, and in that form we always meet it in every day life.

I have already demonstrated to you that silver dissolves in nitric acid, and on repeating the experiment with copper, you perceive that this metal also dissolves, yielding a bluish green solution of copper nitrate. If then we dissolve, say, a coin in nitric acid, we should obtain a liquid containing a mixture of silver and copper nitrates, such a liquid as, in fact, you see in this flask in which a sixpence has been dissolved in the smallest possible quantity of strong nitric acid.

The change brought about by the acid upon the silver and copper respectively may be represented by the equations—



How, then, can we separate the silver from the copper in such solutions, or, to put the matter in other words, how can pure silver nitrate be made from coin? To answer this question, I place in these two tubes pieces of silver and copper nitrates respectively, and gently heat the tubes, side by side, over the Bunsen burner, when, as you see, the copper nitrate very soon blackens and decomposes, whilst the silver nitrate experiences no alteration, unless the temperature is raised to a very high degree. The copper nitrate has, in fact, been decomposed into copper oxide, nitrogen peroxide, and oxygen, in accordance with the equation  $\text{Cu}(\text{NO}_3)_2 = \text{CuO} + \text{NO}_2 + \text{O}$ .

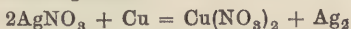
Now, black copper oxide is insoluble in water, and it follows from all this that if I evaporated down my mixed solution of silver and copper nitrates, and then gently heated the solid residue, all the copper

nitrate would be decomposed, leaving the silver nitrate intact, and on treating the mass with water the silver nitrate would dissolve out, leaving the copper oxide behind. To show you how the operation is carried out in practice, I have in this evaporating dish some blue crystals containing silver and copper nitrates. Gently heating the dish over the burner whilst I keep at the same time the contents well stirred with this glass rod, you perceive that the mass is blackening. Taking out a little on the point of the rod I add it to some strong ammonia, when the blue colour bears evidence to the fact that some copper nitrate is still present. Continuing to heat the mass for five minutes longer I now again remove a sample and test it with the ammonia, when, as you see, no blue colour is perceived, showing that all the copper nitrate has been decomposed into copper oxide. Now, pouring boiling water over the residue, and passing the whole through a filter, I obtain a colourless solution, containing all the silver nitrate, and from which I could obtain it in the solid form by evaporating down the liquid.

There are, however, several other means of arriving at the same result.

Pouring some strong nitric acid over the copper nitrate in this tube, you perceive that it is completely soluble therein, but, repeating the experiment with the silver nitrate in the next tube, little, if any of it, dissolves. It follows, therefore, that if I gently evaporated my solution of mixed silver and copper nitrate to dryness, and then washed the solid residue with strong nitric acid as long as the acid continued to be coloured blue, I should wash away all the copper nitrate and leave the silver nitrate intact.

Placing a piece of sheet copper in this solution of silver nitrate, you see that we immediately get a black deposit upon its surface. This latter metal has, in fact, exchanged places with the silver, which is consequently precipitated on the copper in accordance with the equation—



If, then, I placed pieces of copper in the mixed solution of silver and copper nitrates, the silver would be thrown down as a black powder. This I could collect, wash free from copper nitrate, and redissolve in nitric acid, obtaining in this way silver nitrate free from copper.

Silver chloride is, as you remember, insoluble in water, and is produced when a solution of, say, common salt is added to one of silver nitrate, but copper chloride, on the other hand, is soluble in water.

If, for instance, I add common salt to this solution of silver nitrate, all the silver is thrown down as silver chloride, but, on adding common salt to this solution of copper nitrate, no precipitate is formed. It follows therefore that, if I add common salt to a mixture of silver and copper nitrates, say the remainder of the solution obtained by dissolving the sixpence in nitric acid, I throw

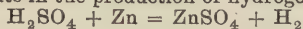


down all the silver as silver chloride, whilst the copper remains in solution. Taking then the solution I add one of common salt to it so long as a precipitate occurs, and then transfer the whole to a paper filter supported in a funnel. On this the insoluble silver chloride is caught, whilst the soluble copper nitrate passes through, and now, washing the precipitate with boiling water until the liquid which passes through ceases to give a blue colour with ammonia (denoting the absence of copper), I have on the filter all the silver as pure silver chloride. The next operation is to convert it into silver nitrate. It would be useless to attempt to do so by adding it to nitric acid, since silver chloride is insoluble in that liquid.

I must, in fact, convert the silver chloride into metallic silver, and then dissolve the metal in the acid.

To effect this we may either reduce the chloride by nascent hydrogen, or fuse it with sodium-potassium carbonate.

To carry out the first method, I place the moist chloride in this larger beaker and cover it with granulated zinc. Next pouring some water over the mixture, I acidulate the water with sulphuric acid. Under these circumstances the reaction between the acid and the zinc results in the production of hydrogen thus—



and the hydrogen at the moment of its liberation from the acid combines with the chlorine of the silver thus—



The spongy substance into which, as you see, the silver chloride is being converted is, in fact, metallic silver.

When the action is complete, which we insure by adding sufficient zinc (at least 65 parts by weight being, as the equations tell us, necessary for every 216 parts by weight of silver, or for every 287 parts by weight of silver chloride), the excess of zinc is then dissolved away by a little more sulphuric acid, and the silver so obtained washed free from zinc and dissolved in nitric acid.

It will be instructive for us to pause a moment to enquire in what way the hydrogen acts in this reaction.

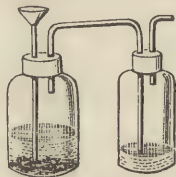


FIG. 52.—PURE HYDROGEN WITHOUT ACTION UPON SILVER CHLORIDE.

I have in one of these flasks (fig. 52) some zinc and water, and pouring some sulphuric acid over the mixture hydrogen gas is



liberated, and is purified by passing it through a solution of caustic soda contained in the wash bottle. Connecting a piece of rubber tubing to the exit of the latter, I cause the gas to bubble up through this test tube containing silver chloride suspended in water, and you perceive that no trace of blackening occurs.

Ordinary hydrogen, prepared in a separate vessel, cannot in fact attack silver chloride, but if the hydrogen is liberated in actual contact with the silver chloride then decomposition ensues.

Now there is good reason for believing that the molecule of hydrogen gas contains two atoms. When we prepare the hydrogen as I have just done, these atoms are *in the immediate vicinity of the zinc* in the act of uniting with each other, but above the surface of the liquid they have already done so.

So that in the tube, when hydrogen was caused to bubble up through silver chloride, we had molecules of hydrogen in contact with molecules of silver chloride; but when the zinc was *in contact* with the silver chloride we had atoms of hydrogen acting upon molecules of silver chloride.

Now in a molecule the constituent atoms are in a position of stable equilibrium, requiring some force to separate them, but the atoms themselves, if free, will tend to combine with a substance, or to produce decompositions which, as molecules, they would be incompetent to effect.

This state of affairs, in which the atoms are separated from each other, is called the nascent state of the element in question, and we shall subsequently have reason to revert to this matter in explaining the changes which go on during development.

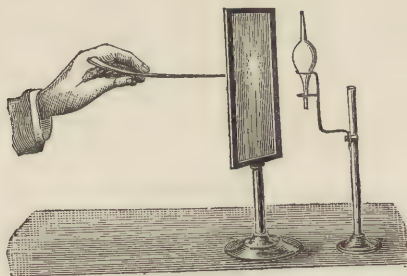


FIG. 53.—EXPLOSION OF MIXTURE OF HYDROGEN AND CHLORINE.

As illustrating the intense affinity which chlorine possesses for hydrogen, and in virtue of which the separation of silver from silver chloride is accomplished, I have in this thin glass bulb (fig. 53) a mixture of the two gases, and on burning in front of it

a short piece of magnesium wire the bulb is shattered to pieces. Here the increased vibration of the molecules of chlorine, brought about by their absorbing the radiant energy of the source of light, results in separating the atoms to a greater distance from each other, and this brings about their combination with the hydrogen in intimate contact with them.

Another method of converting silver chloride into metallic silver is to fuse it with potassium-sodium carbonate. I have here some dry silver chloride, and, mixing it in a mortar with twice its weight of mixed sodium and potassium carbonate, I place the mixture in this small crucible, and heat the whole to intense redness for fifteen minutes in this gas furnace, under which circumstances the silver chloride will be acted upon by, say, the sodium carbonate in accordance with the equation—



the silver remaining at the bottom of the crucible as a button of the metal.

The sole use of the potassium carbonate in the operation is to lower somewhat the melting point of the sodium carbonate, and so enable the reaction to take place at a lower temperature.

It is frequently a question in practical work of recovering silver from paper clippings. To do this it is merely necessary to burn away the paper, and then to dissolve the residue in nitric acid.

Fixing baths contain, as you know, a considerable quantity of silver, and we must next learn how this can be extracted from them.

The action of a fixing bath, whether of hypo or cyanide, depends upon the fact that either of these substances will dissolve the silver haloids.

In these tubes I have portions of silver chloride, bromide, and iodide respectively, and adding to each a solution of hypo, you perceive that in each case the haloid dissolves in the fixing salt.

It follows from this that common salt added to a fixing bath will not precipitate silver chloride, since this substance is soluble in hypo or cyanide. We must, in fact, to separate out the silver convert it into some form in which it is insoluble in hypo or cyanide.

Two methods are open to us to effect this.

To illustrate the first I place this sheet of bright copper in a fixing bath, and you perceive that its surface becomes white, the solution meanwhile becoming blue.

The copper has acted, in fact, upon the hypo in a similar way to the manner in which it acted upon silver nitrate, the copper itself dissolving in the hypo and the silver being thrown out of solution.

To precipitate the silver from old fixing baths we might, therefore, place pieces of sheet copper in them, collect the silver, wash it free from everything soluble with boiling water, and then redissolve it in nitric acid and so obtain silver nitrate.

Adding some ammonium sulphide to a solution of silver nitrate we get, as you see, a black precipitate. This is silver sulphide, represented by the formula  $\text{Ag}_2\text{S}$ , and adding hypo to it you perceive that it is insoluble therein.

You will readily understand, therefore, that by adding ammonium sulphide to old fixing baths we can precipitate all the silver as black silver sulphide, and this can then be collected and converted into silver nitrate.

Here I have some of this black substance, and adding nitric acid to it you see that it dissolves. It might seem at first sight that the solution contained silver nitrate, but this is not the case, some of the sulphur of the silver sulphide having, in fact, been oxidised by the nitric acid into sulphuric acid, with the result that the liquid really contains a mixture of silver nitrate and sulphate.

To convert the silver sulphide into metallic silver we may fuse it, as before, with sodium-potassium carbonate, but a simpler plan consists in mixing it with an equal volume of the following: Flour of sulphur two parts, nitre four parts, fine dry sawdust two parts.

Such a mixture I have here in this crucible, and applying a lighted match to the top of it, vigorous combustion ensues, at the conclusion of which we get, as you see, the whole of the silver as a brilliant metallic button at the bottom of the crucible. The mixture is, in fact, its own combustible and supporter of combustion in one, the nitre furnishing the oxygen necessary for combustion, and in this the charcoal and sulphur burn, and the nitre, becoming converted into probably potassium oxide, then reacts upon the silver sulphide, converting this latter into metallic silver, with the simultaneous production of potassium sulphide.

#### SUMMARY.

*Nitric acid converts silver and copper into their nitrates. Copper nitrate is readily decomposed by heat into copper oxide and other products. Silver nitrate decomposes with greater difficulty. Ammonia strikes a blue colour with solutions of copper. Copper nitrate is very soluble in strong nitric acid, silver nitrate is comparatively insoluble in it.*

*Metallic copper precipitates silver from its solutions. Copper chloride is soluble in water, silver chloride is insoluble in that liquid.*

*Atoms at the moment of their combination with each other to form molecules can bring about changes which the molecules are unable to effect. Ordinary hydrogen is without action on silver chloride, nascent hydrogen decomposes it. Greenish yellow chlorine absorbs white light, which consequently causes a mixture of this gas and hydrogen to combine with explosion.*

*Silver chloride or sulphide are converted into metallic silver when fused with sodium carbonate.*

*Silver sulphide is insoluble in hypo or cyanide.*

## LECTURE XVIII.

PREPARATION, PROPERTIES AND PHOTOGRAPHIC USES OF GELATINE, ALBUMEN, PYROXYLINE, ETHER AND ALCOHOL—MANUFACTURE OF GELATINE FROM BONES AND HIDES—EFFECTS OF VARIOUS REAGENTS UPON IT—PREPARATION OF ALBUMEN FROM EGGS AND BLOOD SERUM—CELLULOSE AND ITS NITRATES—EXPLOSIVE GUN COTTON AND PHOTOGRAPHIC PYROXYLINE—ACTION OF DIASTASE UPON STARCH AND OF YEAST UPON MALTOSE—DEHYDRATION OF ALCOHOL—MANUFACTURE OF ETHER FROM IT.

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GELATINE, albumen, and pyroxyline are the substances employed as vehicles to keep the layer of sensitive silver haloid, etc., on the surface of its support, and this being the case it will be convenient at this point to study their properties, as well as those of the solvents used with them.

Chemically speaking, gelatine is a mixture in variable proportions of two substances of indefinite composition, viz., chondrin and glutin, and is prepared from either bones or hides.

To illustrate its preparation from bones, I placed in this glass vessel, about a fortnight since, the thigh bone of a fowl; and now, decanting off the acid, you see that the originally brittle and hard solid has become quite soft. The acid has, in fact, dissolved out the calcium phosphate originally present in the bone, and has left unchanged a substance termed ossein. To the calcium phosphate the bone owed its original hardness, its toughness being due to the ossein.

In this other vessel some ossein, freed from acid by repeated washing, has been boiled for six hours with water and then permitted to cool, and you see, that by so doing, we have produced a jelly, derived from the ossein by its gradual conversion into the mixture of chondrin and glutin, commonly called gelatine. It would be quite easy to slice up this jelly into shreds or fine filaments, and these on drying would become converted into the semi-transparent solid form in which gelatine is generally met with.

To prepare gelatine from hides these are submitted to a series of operations to free them from blood, hair, &c., and the purified product is then converted into gelatine by long continued digestion in warm water.

Placed in cold water gelatine swells, as you will see by comparing the volume of this drachm of dry gelatine with that of the same weight of the substance at the bottom of the water in



the next vessel, and when I heat the mixture you see that the gelatine readily dissolves.

Upon the relative proportions of gluten or of chondrin present in a sample of gelatine, its value for a given kind of photographic work depends, and I must therefore illustrate how this is determined.

I have here two samples of gelatine dissolved in the same quantity of water, and adding to each an equal volume of a strong solution of chrome alum, you see that one sample at once stiffens to a jelly, whilst the other remains practically unchanged. The gelatine whose solution was so changed by the chrome alum, contains relatively more chondrin than the other, and such a gelatine would be specially suited for emulsion making, whilst the other sample would be best for photo-mechanical work, or indeed for any process dependent for success upon the possibility of readily dissolving away the gelatine.

In another vessel I have what was a week ago a stiff jelly of gelatine, but now you see that the mass is almost as mobile as water. Gelatine will in fact slowly decompose in contact with water, and eventually completely lose its property of setting.

Owing to the presence of chondrin in all gelatines these will be rendered insoluble to a greater or lesser degree when brought in contact with ordinary white alum or with chrome alum. To illustrate this point, half a sheet of gelatine has been soaking in a strong solution of chrome alum for half an hour, and on placing it, together with the other half of the original sheet, in hot water, you perceive that one dissolves and the other does not. The precise nature of the change does not appear to be well understood, but is probably due to the formation of an insoluble compound of the chondrin and the chromic oxide of the chrome alum.

In this case, the gelatine is stained more or less, but in the other sample, which has been soaking in ordinary alum, the gelatine has, as you see, retained its original colour.

Pouring some bromine water into this solution of gelatine, I obtain a reddish brown precipitate, and we learn from this that gelatine precipitated that element, and adding silver nitrate to another portion of the same solution of gelatine, a white precipitate bears evidence to the fact that some change has again occurred. Light changes the precipitate given with silver nitrate to a brick red colour.

From these experiments you will be in a position to learn of what great value gelatine is to the photographer.

Let us suppose, for instance, that I wished to coat the surface of this sheet of paper with silver chloride. To do so I should float it on a solution of gelatine and common salt in water, and when the gelatine was quite dry I should float the prepared surface on a solution of silver nitrate. Double decomposition would then set in, and I should have a layer of silver chloride on the surface of the paper. If I had used a plain solution of sodium chloride this



would sink into the paper and the silver chloride formed when the paper was floated on silver nitrate would follow suit, the result being that the positive print made on paper so prepared would have a sunken-in appearance, as you can see in the sample before you. By mixing, however, the common salt with gelatine, I prevent the sinking-in of the solution and so obtain a much better final result, as will be seen by comparing this print with the former one. Albumen, another substance used for similar purposes, occurs in blood serum and in white of egg.

To prepare it from the latter substance the white of egg is mixed with some water and beaten to a froth, an operation conveniently carried out on a small scale by placing the mixture in a bottle with some broken glass and vigorously shaking the whole. When subjected to this treatment the cellulose enclosing the albumen are broken, and the substance escapes, yielding a turbid solution. If, however, this is filtered a clear liquid results.

Pouring some silver nitrate into a solution of albumen you perceive that an insoluble precipitate forms. This is a compound analogous to that obtained with gelatine, and, like the latter, reddens on exposure to light, to illustrate which change I have here a print made on it.

You will at once understand, therefore, that if I made a mixture of albumen and common salt, and floated paper upon this mixture, and then, when dry, again floated the paper on a solution of silver nitrate, the albumen would, like the gelatine, keep the sensitive coating on the surface. It is fortunate in this connection that silver nitrate coagulates albumen, for if it did not it would be impossible to employ that substance in the manner just indicated. To illustrate this effect I float two pieces of paper coated with albumen, one upon plain water and the other upon a solution of silver nitrate, when you perceive that the albumen coating is dissolved off in the one case and remains unaffected in the other.

Cellulose, of which we have an example in cotton wool and in fine white blotting paper, differs from albumen and gelatine in being a definite chemical compound, represented by the formula  $(C_6H_{10}O_5)_n$ , a substance completely insoluble in water, alcohol or ether.

By treating cellulose with nitric acid it becomes converted into a series of organic nitrates, the particular nitrate or nitrates formed depending on the strength of the nitric acid, on its temperature, and on the time of immersion.

Sulphuric acid possesses an intense affinity for water, as is evidenced by the fact that heat is liberated when the two are mixed. To illustrate this point I pour some strong sulphuric acid into its own volume of water, and the steam which arises from the mixture is sufficient evidence of the rise in temperature which has occurred. Since, as a rule, the nitric acid we employ is too weak to change cellulose into these organic nitrates, we commonly mix it with sulphuric acid, and immerse the cellulose in the mixture.

The main function of the sulphuric acid is doubtless to dehydrate the nitric acid, but there is reason to believe that it also brings about certain secondary reactions, the considerations of which would, however, lead us too far from our present subject.

To illustrate the formation of these organic nitrates I have in this beaker, cooled down to  $0^{\circ}$  C. by being placed in melting ice, a mixture of three volumes of strong sulphuric acid and one volume of the strongest fuming nitric acid (spec. grav. 1.52), and in this mixture I place a small piece of purified cotton wool.

Whilst the foregoing experiment is progressing, I will make another organic nitrate in a different way. In this second beaker, the contents of which are heated to about  $70^{\circ}$  C. by being placed in hot sand, is a mixture of 12 fluid ounces of strong sulphuric acid, four fluid ounces of nitric acid of specific gravity 1.45, and 17 drachms of water, and in this mixture I place 270 grains of cotton wool in small successive quantities at a time (fig. 54).



FIG. 54.—PREPARATION OF PYROXYLINE.

Reverting now to our first beaker, I remove a piece of the material with a glass rod and plunge it into a basin of water. Tearing it in my fingers you see that the original structure of the cotton-wool is only very slightly altered, and placing some of the material from which the greater part of the water has been removed by squeezing it between folds of blotting paper in a mixture of alcohol and ether, you see that it is almost completely insoluble therein. I have, in fact, converted the cellulose into its highest nitrate, viz., cellulose-hexanitrate, represented by the formula  $C_{36}H_{42}O_{12}(ONO_2)_{18}$ .

Turning now to the second beaker, I remove the material and plunge it into water, when, on tearing it with my fingers, you

perceive that the original structure of the cotton-wool is almost completely lost, and placing some of it in a mixture of alcohol and ether you perceive that it is completely soluble therein.

I have, in fact, in this case converted the cellulose into a mixture of cellulo-tetra and trinitrin, represented by the respective formulæ  $C_{36}H_{42}O_{12}(OH)_6(ONO_2)_{12}$  and  $C_{36}H_{42}O_{12}(OH)_9(ONO_2)_9$ , and this mixture constitutes photographic pyroxyline, its solution in alcohol-ether forming collodion. As prepared for iodised collodion the quantity of trinitrin exceeds that of the tetranittrin.

If I had permitted the cotton-wool to remain a long time, say 12 hours, in contact with the mixture, then the greater part of the product would consist of the tetranittrin mixed with very little trinitrin, and such a mixture, although still soluble in alcohol-ether, would yield a collodion too horny and repellent to be of use for negative work, although excellent for enamelling.

We have next to deal with the solvents used for pyroxyline, viz., alcohol and ether.

Starch, or any substance containing it, such as barley, wheat or rice, becomes converted, in contact with diastase (a nitrogenous substance contained in germinated grain), into maltose or malt sugar, and this latter is changed by yeast into alcohol and carbon dioxide.

To illustrate these points, I yesterday placed in this bottle a small quantity of starch paste mixed with some diastase, and kept the whole overnight on the kitchen hob. Boiling some of it with this solution of copper oxide in ammonia, you perceive that a red precipitate forms, a test which, we know, characterises maltose and many other sugars.

Repeating the experiment with ordinary starch, you perceive that no change takes place, showing us that no maltose is present.

To illustrate the action of yeast in converting maltose into carbon dioxide, there was placed yesterday, in the large retort which you see, a mixture of maltose and yeast, and, as you observe, a jarful of gas has collected in the receiver placed over the pneumatic trough, which gas will extinguish the taper I plunge into it, being, in fact, carbon dioxide, and on removing the stopper from the retort I am made conscious, by the vinous odour, that alcohol is present.

To free the alcohol from water, we must, however, subject it to distillation. To do this I connect (fig. 55) the retort with a flask immersed in cold water, and heat the contents, when the alcohol being more volatile than the water, passes over first.

Alcohol so prepared is not, however, sufficiently free from water to render it of use for photographic purposes.

To remove the remainder of the water, it is necessary to mix it with quicklime, and subject the mixture to re-distillation. The lime in this case combines with the water to form slaked lime, and so removes it.

In addition to its use in making collodion, alcohol is employed

for rapidly drying gelatine negatives, and for freeing gelatine emulsion from water—uses which its affinity for water enables it to fulfil.

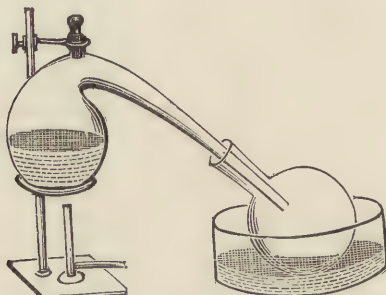


FIG. 55.—DISTILLATION OF ALCOHOL.

When wood is subjected to destructive distillation in closed vessels, it gives, amongst other things, tar, acetic acid and wood naphtha. This latter contains methylic alcohol, mixed with impurities, and a mixture of the crude compound with ordinary alcohol constitutes methylated spirit. This substance answers well for every photographic purpose, excepting the preparation of collodion.

When sulphuric acid is carefully mixed with alcohol in certain proportions it converts the alcohol into ethylic sulphate, in accordance with the equation  $C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O$ , and at a temperature of about  $60^\circ C$ . this ethylic sulphate will combine with more alcohol to form ether and sulphuric acid, thus— $C_2H_5HSO_4 + C_2H_5OH = C_2H_5OC_2H_5 + H_2SO_4$ .

It will be thus perceived that a small quantity of sulphuric acid will convert a large quantity of alcohol into ether, and this fact is made use of to prepare the latter substance. In this flask (fig. 56) was placed a mixture of 12 ounces of methylated spirit and 10 ounces of strong sulphuric acid, the level of the liquid being marked by a piece of paper gummed on the outside of the flask.

When the mixture was heated the ether distilled off and was condensed in the Liebig's condenser, and to keep up the supply of alcohol the left-hand tube connected to the bottle containing alcohol was blown through from time to time.

As you perceive, several ounces of ether have collected in the receiver, but this liquid is by no means pure enough for photographic purposes, as it contains sulphurous acid, alcohol and water. To free it from these I shake it up with caustic soda, which gets rid of the former impurity, and the alcohol and water



are then removed by re-distilling the liquid over fused calcium chloride.

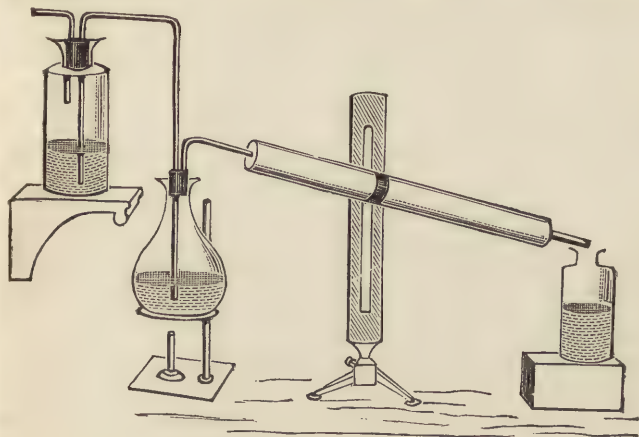


FIG. 56.—MANUFACTURE OF ETHER.

A mixture of equal parts of alcohol and ether dissolves pyroxyline, and such a solution constitutes plain collodion, about six grains of pyroxyline being employed for every ounce of the mixture.

I have here some plain collodion, and pouring it on glass and returning the excess to the bottle, the ether and alcohol soon evaporate, and leave, as you see, on the glass a very fine and almost structureless film of the pyroxyline.

By mixing the collodion with certain chlorides, iodides or bromides, these salts would remain in the film on the glass, and would subsequently become converted into silver chloride, iodide or bromide on immersing the film in a solution of silver nitrate. Evidently only those haloid salts can be used which are soluble in alcohol-ether, the salts generally employed being those of ammonium, cadmium or zinc.

#### SUMMARY.

*Ossein*, contained in bones, cartilage, connective tissue, sinews and skin, is converted by long continued boiling into the mixture of *chondrin* and *glutin* commonly known as *gelatine*.

*Gelatine* is soluble in hot but insoluble in cold water.

Ordinary white or chrome alum render *gelatine* insoluble in hot water.

*Silver nitrate* and *bromine* combine with *gelatine*.

*Albumen* is contained in white of egg and in blood serum.



*Silver nitrate* combines with *albumen*, and the compound, white at first, becomes red on exposure to light.

*Nitric acid* coagulates *albumen*.

*Cellulose* is contained in cotton wool, paper, rags, &c.

*Cellulose* acted upon by *nitric acid* becomes converted into one or more *cellulo-nitrins*.

*Cellulose hexanitrin* is explosive gun cotton, and is insoluble in alcohol-ether.

The mixture of *cellulo tri* and *tetra nitrin* constitutes photographic *pyroxyline* soluble in alcohol-ether.

If the *tetra nitrin* predominates, the *pyroxyline* is of little use to make iodised collodion.

The solution of *pyroxyline* in alcohol-ether, poured on glass, leaves behind a film of *pyroxyline*.

Iodised (so called) collodion is a solution of certain chlorides, iodides, or bromides in plain collodion.

Starch is converted by *diastase* into maltose, this latter by yeast into alcohol.

Alcohol is freed from much water by simple distillation, from smaller quantities by distillation over lime, potassium carbonate or calcium chloride.

Alcohol heated with a certain quantity of sulphuric acid yields ether.

## LECTURE XIX.

THE WET COLLODION PROCESS—NECESSITY FOR A CLEAN SUPPORT FOR THE FILM—USE OF SUBSTRATUM—COMPOSITION OF COLLODIONS AND OF THE SILVER BATH—USES OF IODIDES AND BROMIDES IN COLLODION—GRADUAL WEAKENING OF THE SILVER BATH—NECESSITY FOR THE PRESENCE OF CERTAIN SUBSTANCES IN THE FILM—PRODUCTION OF NEGATIVE OR POSITIVE COLLODION IMAGES.

THE following two formulæ given by Abney\* will serve as types of collodions containing a soluble iodide only, or both iodide and bromide:—

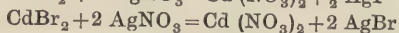
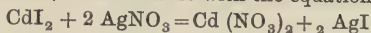
### PLAIN IODISED COLLODION.

Cadmium iodide	..	..	..	5 grains.
Plain collodion	..	..	..	1 ounce.

### BROMO-IODISED COLLODION.

Cadmium iodide	..	..	..	4½ grains.
Cadmium bromide	..	..	..	2    "
Plain collodion	..	..	..	1 ounce.

If a plate coated with either of the above collodions is immersed in a solution of silver nitrate, the cadmium iodide or iodide and bromide become converted into silver iodide or a mixture of silver iodide and bromide, in accordance with the equations—



the insoluble or comparatively insoluble silver haloids remaining in the film, and the soluble cadmium nitrate mixing with the solution of silver nitrate.

A reference to the frontispiece will show for what special purpose each of these collodions is suitable. Thus, since silver iodide is less sensitive to light than silver bromide, if the first formula is used, a comparatively long exposure will be required to enable the shadows of the picture which reflect very little light to impress themselves, and this will result in the high lights being over exposed. On development the effect will make itself visible as exaggerated density in the high lights with partial obliteration of the detail present in them. This traced to its source will be found to depend upon the fact that light reflected by darker portions of any view is less blue than that reflected by its high lights, and to

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\* "Instructions in Photography," pages 71 and 72.

these blue rays silver iodide is comparatively insensitive. If, on the other hand, bromide had been used alone, the negative would be more or less flat owing to the superior sensitiveness of the bromide to comparatively feeble light. If, however, both salts are combined, we get the advantage of the superior sensitiveness of the bromide combined with the increased density in the high lights due to the iodide.

In copying book illustrations, drawings, etc., for photomechanical and other purposes, where the object is to obtain excessive density and perfectly clear shadows, a collodion containing an iodide only is most suitable, but for ordinary positive or negative work some bromide must be present. I will illustrate these facts by projecting on the screen transparencies made from three negatives, one taken with collodion containing iodide only, the next with collodion containing bromide only, and the last with collodion containing both iodide and bromide, and to show the superiority for certain kinds of work of a collodion containing iodide only, I next project on the screen two negatives of the page of a book, one made from a collodion containing iodide only, and the other from one containing iodide and bromide.

As regards the glass plate itself, it is evident that it must be perfectly clean, for, as we shall learn in the next lecture, the slightest speck of dust or dirt will form the nucleus of a stain.

A glass plate in its usual condition is generally greasy and dusty, and we require, to clean it, a mixture which will remove both these things. Such a mixture is found in any fine impalpable powder—say French chalk—mixed with alcohol and ammonia. The ammonia converts the grease into soap, and this the alcohol dissolves, whilst the fine powder mechanically carries away any dust which may be present on the glass.

To illustrate the action of the ammonia, I place in this dry test tube a drop of olive oil, and then add some ammonia to it, when you see that we obtain a milky liquid, an ammonia soap in fact. Adding to this some alcohol, you see it dissolves therein, and the tube washed out with water exhibits no signs of greasiness.

Evidently if we remove the grease and dirt *fairly well*, and then interpose between the surface of the glass and the pyroxyline film a very thin layer of, say, gelatine or albumen, we shall obtain negatives free from stain, although the glass may have been in the first instance far from being as clean as if polished with French chalk, alcohol and ammonia.

Many excellent operators prefer, in fact, giving the plate a substratum, as it is called, after having permitted it to soak for some time in a ten per cent. solution of caustic soda.

As examples of such substrata, the following are appended:—\*

GELATINE SUBSTRATUM.					
Gelatine	..	..	..	..	75 grains.
Water ..	..	..	..	..	60 ounces.
Ammonia	..	..	..	..	2 drachms.

\* Leaper, "Materia Photographica," p. 204.

## ALBUMEN SUBSTRATUM.

Albumen	..	(white of one egg)	1 ounce.
Water	..	..	20 ounces.

The plate, either perfectly clean or else coated with a substratum, is then coated with collodion, being held whilst so doing by the tips of the fingers, or better, in a pneumatic holder (fig. 57).

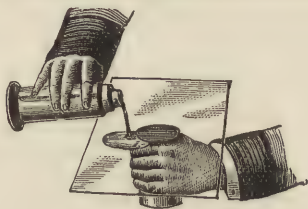


FIG. 57.—COLLODIONISING A PLATE.

If it was at once immersed in the bath the film would probably leave the plate, whilst if the collodion were permitted to dry for too long before immersing the plate in the solution of silver nitrate the resulting film of silver haloid would be comparatively insensitive. The former result is due to the comparative softness of a film which has just set, the latter to the contraction which occurs on drying and the consequent loss of porosity.

For these reasons from one to six minutes are permitted to elapse between the time the collodion has ceased dropping and its immersion in the bath.

There are, however, certain points to be attended to in the preparation of the latter solution which I must now deal with.

Placing in this tube some solution of silver nitrate I add to it a drop of a rather dilute solution of cadmium iodide, and you see that the usual precipitate of silver iodide falls, but now filling up the tube with more solution of silver nitrate you perceive that the precipitate has disappeared.

Silver iodide is, in fact, soluble in a solution of silver nitrate.

It follows from this that, if a film containing a soluble iodide was immersed in a solution of silver nitrate, a portion of the silver iodide first formed would be dissolved out, resulting in minute white spots in the negative, these being places containing no sensitive silver salt.

To avoid this mishap the bath must be saturated with iodide before commencing work, and obviously the simplest way to effect this is to coat a plate with collodion and leave it in the bath for an hour or so. Once saturated with silver iodide the bath cannot, of course, dissolve any more.

It is evident that every plate sensitised in the bath will deprive it of a certain quantity of silver nitrate, and knowing the quantity

of collodion requisite to coat a plate of a given size, and the reaction which occurs, it is easy to calculate how much silver nitrate a given quantity of the bath still contains after a certain number of plates have been sensitised in it.

Let us suppose that we are using a collodion containing 5 grains of cadmium iodide to the ounce, and a 40-grain bath. Now, 20 minims of collodion will cover a quarter-plate, and this quantity will contain .208 grains of cadmium bromide. From the equation previously given, we learn that 366 parts by weight of cadmium iodide will combine with 340 parts by weight of silver nitrate, therefore, the quantity of silver nitrate which will combine with .208 grains of cadmium iodide is given by the proportion  $366 : .208 :: 340 = .186$  grains.

Every quarter-plate that we sensitise removes, then, this quantity of silver nitrate from the solution, and this means that if we took, say, 10 ounces of bath solution at starting, no free silver would be present after sensitising  $\frac{400}{.186} = 2,150$  quarter-plates.

But we have another point to consider, viz., the fact that each plate sensitised removes from the bath a certain quantity of silver nitrate in the solution which wets its surface, a quantity about equal to 5 minims per square inch. Now, in 10 ounces there are 4,800 minims, and this quantity would therefore be used up by a surface of 960 square inches. Taking now the area of a quarter-plate as 14 square inches, we see that  $\frac{960}{14} = 68$  quarter-plates would use up that quantity of bath by removing the liquid mechanically. In consequence of this we may rest assured that a bath solution, so long as it will wet the plate, will always contain sufficient silver nitrate to sensitise it.

Evidently the collodionised plate must remain in the bath until all the soluble haloid has been converted into silver haloid. The actual length of time which it takes to bring about this change will depend upon the strength of the bath, the strength of the collodion, and the temperature. The stronger the bath, the weaker the collodion, and the higher the temperature the shorter the time of immersion, and *vice versa*.

With a collodion and bath of the given strength and in summer, about three minutes immersion should suffice, but in winter this may become six minutes, with the same solution.

Since the solution of silver nitrate becomes gradually weaker and weaker the more plates are sensitised in it, it follows that a plate must be left for a longer time in an old bath than a new one.

The change of soluble into insoluble silver haloid is accompanied as you see by a change in the appearance of the plates, which, quite transparent before immersion, becomes translucent when sensitised.

Since we immerse our collodionised plates in the bath before all the ether and alcohol have evaporated, it is evident that these



substances are introduced into the solution of silver nitrate, as well as the cadmium or other nitrate resulting from the interaction of the soluble iodide or bromide and the silver nitrate.

So far as the cadmium or other soluble nitrate is concerned, no great harm is done, but it is far otherwise with the ether and alcohol, which, by their presence in the bath, produce a series of vertical markings on the finished negative.

Another trouble arises from the silver iodide in the bath, which accumulating in a solution which has been in use for some time is precipitated on the plate as a number of minute granules, which, as they wash off in the subsequent operations leave more or less transparent spots on the film.

To illustrate how the excess of silver iodide may be removed from the silver nitrate bath, I dilute some silver nitrate saturated with silver iodide with a considerable quantity of water and the milkiness produced is the silver iodide thrown out of solution. Silver nitrate, in fact, dissolves silver iodide only on condition that it is sufficiently concentrated.

Ether and alcohol being volatile escape when a bath solution is boiled down, and it follows from these facts that to improve an old bath it is only necessary to dilute it with, say, four times its volume of water and filter out the precipitated iodide, after which the solution is boiled down to its original bulk. Ether and alcohol being more volatile than water will escape with the first portions of the steam and the boiled bath will be at the conclusion of the experiment quite free from these substances.

The collodion film is exposed either whilst wet with a solution of silver nitrate or coated with a layer of certain other substances.

To illustrate the necessity for this, I turn on the red light and prepare an iodide collodion plate in the ordinary way. Having done this I wash it under the tap to remove the greater portion of the silver nitrate, and to ensure the removal of the remainder I dip the film in a strong solution of potassium iodide, which convert the traces of silver still remaining in the film into silver iodide. After having again washed the plate to remove the potassium iodide, I make a cross upon it with a strong solution of silver nitrate and then exposing it for a minute to the light emitted by our magnesium lamp I place it in the developer, when you see that the cross has developed up black on a white ground. The silver nitrate has here played the part of what we call a sensitiser, *i.e.*, it has resulted in conferring increased photographic sensitiveness upon those portions of the plate containing it, the action being due either to the fact that by its presence it facilitates the conversion of the insensitive allotrope of silver bromide into the sensitive allotrope, or that it facilitates the actual removal of some of the iodine from its combination with silver iodide.

Most other substances which act as iodine absorbents would produce a similar result, but their action will be discussed in the next lecture.

If we remove the unaltered silver iodide by fixing the plate, and examine it by transmitted light, we see, of course, that the cross appears blacker than the ground; but if we coat the dried plate with a black pigment and examine the whole by reflected light, then the metallic silver which, as we shall subsequently learn, constitutes the fixed image, reflects more light than the black pigment, and we see in consequence a white cross on a black ground.

It follows from this that a negative by transmitted light should become a positive by reflected light, and such is found practically to be the case.

The greater the quantity of white light reflected by the silver constituting the fixed deposit, the better the quality of the resulting positive, and for this reason special precautions, which it would take us too far from our present subject to explain, are taken when a positive is required; these precautions having for their object the production of a metallic deposit of as white a colour as possible.

If the positive photograph is taken on glass then the film side is coated with a black pigment, and the image seen through the glass is not inverted. Instead of glass a thin iron plate covered with a dead black varnish may be employed, but in this case the resulting image is, of course, laterally inverted. A positive produced in this way is called a ferrotype.

#### SUMMARY.

*Collodion contains pyroxyline, ether, alcohol, and (usually) an iodide, or an iodide and bromide soluble in ether-alcohol.*

*The iodides and bromides generally employed are those of cadmium and ammonium.*

*Iodides alone give excessive density but little detail in either high lights or shadows.*

*Bromides alone give detail, but insufficient density.*

*For ordinary negative work the collodion contains a bromide and an iodide.*

*For photo-mechanical work, i.e., the copying of black and white, an iodide only is preferred.*

*Silver nitrate dissolves silver iodide. To prevent it dissolving this from the film itself, some silver iodide is introduced into the bath.*

*Silver iodide dissolved in silver nitrate is precipitated on dilution with water.*

*Too much iodide or too much ether-alcohol in the bath is disadvantageous. These are got rid of by dilution, filtration and evaporation.*

*Every plate sensitised in the bath removes a certain quantity of silver nitrate from it.*

*Silver nitrate, or some substance which will facilitate the action of light upon the silver haloid must be present in the film, which otherwise is comparatively insensitive.*

A collodion *negative* by transmitted light becomes a *positive* by reflected light.

The *whiter* the deposited *silver*, the *better* the *positive* picture will be.

In making collodion *positives* special *precautions* are taken to ensure a *white deposit*, and the *film side* is backed (if glass is used) with a *black varnish*, when we have a non-inverted *positive on glass*; or the picture is made on a *japanned iron plate*, when it constitutes a *ferrotype*. These latter are always *inverted*.

## LECTURE XX.

INSENSIBILITY OF A FILM OF SILVER IODIDE FREE FROM SILVER NITRATE—RESTORATION OF ITS SENSIBILITY BY CERTAIN SUBSTANCES—DRY COLLODION PROCESSES—THE COFFEE PROCESS—EXPLANATION OF THE ACTION OF LIGHT UPON SILVER IODIDE—ANALOGY BETWEEN THE ACTION OF PRESSURE UPON THIS SUBSTANCE, AND UPON YELLOW MERCURIC IODIDE.

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A COLLODION plate, prepared as described in the last lecture, is usually exposed in the camera whilst its surface is wet with a solution of silver nitrate, the object of the latter being, as we already know, to facilitate the change brought about by light.

It might seem at first sight that such a plate would be still utilisable if the film were permitted to dry with the silver nitrate upon it, but such is not the case, for it is found that on drying the silver nitrate crystallises out, and so renders the surface very far from flat, as you see in the specimen before you.

Hence, collodion plates must be exposed very soon after their preparation, and the process is in consequence rather difficult to carry out at a distance from home, as it necessarily involves a dark tent of some sort for sensitising the plate on the spot where it is to be used.

To obviate this drawback, and enable plates to be used some time after their preparation, two methods are open to us. We may prevent the silver nitrate from drying on the film, or we may impregnate the film with some substance which, *when dry*, will enable light to bring about the requisite change.

To carry the first plan into operation we might place in contact with the wet film, as it comes from the bath, a perfectly clean glass plate, with the result that the moisture imprisoned between the two surfaces would prevent the drying up of the liquid and the consequent crystallisation of the silver nitrate. Collodion plates treated in this way can be kept unchanged for many hours, but it will be readily understood that the film is often injured in removing the second glass plate prior to development.

Another method, very frequently used in former years when it was a question of photographing interiors or objects which required a prolonged exposure, was to place in the dark slide, and behind the glass plate, a piece of blotting paper saturated with water. This, by keeping the air in the vicinity of the film very moist, retarded considerably the drying up of the silver nitrate.



Some substances like sugar, syrup, honey and glycerine, dry, as you are doubtless aware, with extreme slowness, and a knowledge of this fact was put to practical use in the early collodion days. Plates sensitised in the usual way were covered with these respective liquids on being removed from the bath, and the silver nitrate was in consequence prevented from drying up for a period of, perhaps, three or four days. Certain nitrates, like those of zinc and magnesium, are deliquescent, *i.e.*, tend to absorb atmospheric moisture, and it will be readily understood that if the collodion was iodised with salts of such metals then sufficient of their nitrates to keep the film moist would soon accumulate in the bath. An exactly similar result would, of course, be obtained by mixing these deliquescent substances with the solution of silver nitrate in the first instance and using the ordinary iodisers.

All these processes mean, however, a *damp* film, and this is evidently far more liable to injury than a dry one, besides being more cumbersome to carry from place to place, owing to the impossibility of packing the plates in contact with each other.

The second method is therefore the most practicable one, and depends upon the fact that certain substances will, applied *dry*, enable light to alter a silver haloid almost as readily as if wet silver nitrate was present.

A large number of substances have been employed for that purpose, such as gelatine, albumen, tannin, pyrogallol, gallic acid, morphine, and even tea or coffee, the action of these latter being due to the theine they contain. Whatever "preservative," as these substances have been called, is used, the plate sensitised in the ordinary way is well washed so as to rid it of every trace of silver nitrate, and then immersed in a solution of the preservative about to be used mixed with sugar, gum arabic, or some such substance in order to facilitate the adherence to the plate of a considerable quantity of the preservative. After having remained for a certain length of time in the solution, the plate is drained and dried and will then keep in good condition for a considerable time.

I will illustrate the process by preparing for you a dry coffee plate.

The collodion I use is the plain iodised one, the formula for which was given in the last lecture, and the bath solution contains 40 grs. of silver nitrate to the ounce. The preservative is made up by boiling 120 grains of ground roasted coffee with 6 ounces of water, filtering the solution and dissolving in it 60 grains each of white gum arabic and of sugar candy.

Collodionising the plate in the usual way I immerse it in the silver nitrate bath, and when sensitised, I remove it and wash it for ten minutes under the tap. Next placing it in the preservative for three minutes, I drain off the solution, and dry the plate by placing it on this piece of sheet iron heated from below by a small gas flame.



It will be readily understood that on account of the fact that the film is first dried and then again wetted during development, special means must be taken to insure the adhesion of the sensitive film to the glass. In fact, chemically clean glass plates, while answering admirably for wet collodion, would not do for "dry" collodion, as this process is called, the want of contact between the surfaces of glass and pyroxiline brought about by the expansion of the film on wetting it making the whole sensitive coating slip off the glass. To avoid this mishap it is indispensable to use an "edging" of indiarubber, or better still, the entire plate is first of all coated with a thin substratum of gelatine such as that mentioned in the last lecture.

If, however, instead of using an iodide, or iodide and bromide in the collodion, a bromide alone was used, then the plates might be washed quite free from silver nitrate, and dried without any preservative, when they would be still capable of being acted upon by light, although to much smaller extent than if a preservative had been used.

But, for reasons which have been already pointed out, the resulting images would be lacking in density, which means that the operation of intensification would have to be made use of after fixation in order to get printable negatives.

If, however, the collodion film is sufficiently thick, and contains a large quantity of silver bromide, then the plates could be developed at one operation by using a suitable developer. This matter will be dealt with subsequently when the question of development is under consideration.

At all events, with silver iodide or with silver bromo-iodide, some preservative is absolutely necessary, otherwise light had little or no action on the plate.

It will be readily understood that with these dry collodion processes the film itself must be very open and porous to enable the preservative to penetrate every portion of it. Pyroxiline eminently suitable for wet plate work would not, in fact, be suitable for dry plate work; what is required being pyroxiline, giving what is technically called a "rotten" film. Such pyroxiline can be obtained by reducing the quantity of water in the formula, given on page 146, to 12 drachms and raising the temperature of the mixture of nitric and sulphuric acid to  $74^{\circ}\text{C}$ .

To illustrate the difference between the two films, I have here two glass plates, immersed in water, coated with films suitable for wet and dry collodion respectively, and you observe that on rubbing one with the finger it comes off in flakes, whilst the other comes off in powder.

This latter would be the one most suitable for dry collodion.

It will be convenient at this point to consider the action of light upon silver iodide. It has been already pointed out that the most probable explanation which can be given of the action of light upon silver bromide for such a length of time as to

yield a developable image, is that light acts in the same way as heat, *i.e.*, converts ordinary silver bromide into that allotrope which fogs on the application of a developer, and it may be here remarked that the same explanation is in all probability true of silver iodide as well.

A comparison of the curves given in the frontispiece show that silver iodide is less sensitive than silver bromide, whilst for chemical reasons it should be more so if the action of light resulted in the separation of the halogen from it. It is, however, well known that whilst silver bromide is readily allotropic, the allotropation of silver iodide is effected with difficulty, and this observed result is in agreement with the markedly smaller sensitiveness to light of the iodide.

The upholders of the chemical theory maintain, however, that the greater sensitiveness of the bromide is due to the fact that pyroxiline, gelatine, albumen, etc., possess a greater affinity for bromine than for iodine. If this was true, then we could increase the sensitiveness to light of any haloid silver salt by placing it in contact with that substance which has the greatest affinity for the halogen. Let us test this conclusion experimentally.

I have here two solutions—one of potassium iodide, and the other of sulphurous acid, both of which absorb iodine fairly well, the potassium iodide converting the iodine into a tri-iodide, represented by the formula  $KI_3$ , and the sulphurous acid becoming oxidised at its expense in accordance with the equation  $H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HI$ . Now if the chemical theory is true, both of these substances should act in a similar way, *i.e.*, they should facilitate the change brought about by the action of light.

To carry out the experiment, I prepare a washed collodion plate, and mark an S on one-half of it with the sulphurous acid, and an I on the other half with the solution of potassium iodide. Now, burning some magnesium in front of the plate, I wash off the solutions and apply a developer, when you see that the ground has darkened more or less, the S appearing as a darker deposit, the I as a less dark one, so that these substances do not act in the same way, although they are both iodine absorbents.

Again, starch and gelatine are both iodine absorbents, but starch is a far better iodine absorbent than gelatine. It would therefore follow, if the chemical theory is true, that starch placed in contact with silver iodide should render it more sensitive than if gelatine had been used.

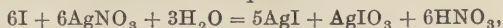
Whilst I have been talking, my assistant has prepared another iodide plate, and has washed it quite free from silver nitrate. I now mark a G on one-half of the plate with a solution of gelatine and an S on the other half with the starch, and this done, I burn some magnesium in front of the plate. On development the G comes out first, in direct opposition to what we should expect.

A number of experiments carried out in this way by Vogel\* conclusively prove the fact that the substance which most energetically absorbs a halogen is *not* necessarily the substance which renders a silver haloid containing that halogen most sensitive on exposure to light—a result which should inevitably hold good if the halogen was actually liberated by a short exposure.

It is often advanced as an argument in favour of the chemical theory that iodine will destroy the image formed by light acting upon silver iodide, it being held that the result is due to the rehalogenisation of the dehalogenised silver salt. That such an effect does occur is doubtless true if the silver salt *has* been dehalogenised, but the result might, in any case, admit of another explanation in view of the experiment of Carey Lea previously quoted. The halogen might, in fact, form a chemical compound with the silver haloid, and so render its allotropation by light more difficult.

It is well known that the image produced upon a wet or dry collodion plate will spontaneously disappear at a certain period after exposure. What explanation can be given of this fact?

Taking the wet collodion process, the chemical theory tells us that the iodine liberated by the halogen is absorbed by the silver nitrate in accordance with the equation—



and that on the removal of the stimulus supplied by light this reaction reverses itself, the liberated iodine being then re-absorbed by the dehalogenised silver salt. That this is the case does not appear, however, to be borne out by the fact that the substance (probably photo iodide) formed by exposing silver iodide to *prolonged* insolation is practically unaffected by nitric acid, and that a silver nitrate bath containing a large excess of nitric acid will not prevent the silver iodide from being altered by light.

Again, the fact that the hydracids, say hydrochloric acid, do not destroy the image is pretty conclusive proof that no halogen has been liberated, and the conclusion is also borne out by the fact that the silver haloids darken beneath the surface of the hydracids.

In this connection it will be useful to remind you that mere pressure will, in non-actinic light, cause silver iodide to fog on the application of a developer. To carry out the experiment I place in this letter-press a dry collodion iodide plate, and put over the centre of it a square piece of ordinary thick white cardboard. Now, screwing down the press so as to subject the portion of the plate beneath the cardboard to considerable pressure, I then release it and develop the whole, when you see that the pressure mark develops up as a square black patch.

The action here is due to the liberation of iodine, or it is not. Now, if iodine is liberated, it is very difficult to understand in what way pressure could facilitate the action, for the

\* "Lehrbuck der Photographie."

volume of gaseous, or even solid, iodine liberated by the decomposition of solid silver iodide should be greater than the volume of the solid which yielded it, and so pressure, instead of facilitating the liberation of the halogen, should actually retard it, if that halogen actually tended to be liberated. If, again, pressure did cause the liberation of the halogen, the same pressure continued for a sufficiently long time should produce a visible darkening just as light does. That this is not the case can be proved by subjecting silver iodide to long-continued pressure for a long time, and noticing that no darkening takes place. Here, for instance, is some silver iodide which has been subjected whilst moist with silver nitrate to a pressure of three tons on the square inch in a Bramah press for three months, and as you see it has not darkened in the least.

But pressure, as you doubtless remember, facilitates in many cases the allotropation of a substance. Here I have some yellow mercuric iodide, and placing it in my letter-press I subject it to considerable pressure, when on removing it you see it has become converted into the red variety of the same substance, the analogy between the effect of pressure on this substance and on silver iodide being thus complete, if we agree that the action of light has resulted in the allotropation of the latter.

We may therefore conclude that light acts upon silver iodide in a similar manner to the way it acts upon silver bromide, viz., that it converts it first into an allotrope capable of being blackened by a developer, and then, if its action is sufficiently prolonged, converts that allotrope into silver photo-iodide.

#### SUMMARY.

*Silver nitrate or some other sensitiser must be present in a silver iodide film if light is to produce any effect upon it.*

*Silver nitrate drying on a film crystallises out and spoils the surface.*

*Many substances like albumen, gelatine, etc., used dry, restore the sensitiveness of an iodide film free from silver nitrate. Such substances are called preservatives or sensitisers.*

*The best halogen absorbent is not necessarily the best sensitiser.*

*Pyroxiline suitable for dry collodion work should give a rotten film.*

*Silver bromide in collodion needs no preservative, but the image is thin and flat when developed by acid development.*

*Silver iodide is practically less sensitive than silver bromide. If the change by light to produce a developable image resulted in the liberation of the halogen, it should be more so.*

*The action of hydracids in not destroying the developable image disproves the chemical theory.*

*Pressure will cause silver iodide to yield a developable image, but no pressure, even in contact with iodine absorbents, will darken it.*



## LECTURE XXI.

COLLODION EMULSIONS—ADVANTAGES OF THE PROCESS OVER DRY COLLODION—NECESSITY FOR AN EXCESS OF SILVER NITRATE—PREPARATION OF COLLO-EMULSION SENSITIVE TO THE INFRA RED—EXPLANATION OF THE RIPENING PROCESS—DIFFERENCE IN SIZE OF PARTICLES OF VARIOUS ALLOTROPES OF SILVER BROMIDE—CURING A FOGGY EMULSION—RESEARCHES OF WARNERKE AND OF STUART WORTLEY.

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IN preparing a dry collodion plate the solution of silver nitrate is merely a means of converting the soluble iodide into silver haloid. Evidently a similar result would be obtained if the silver iodide could be so prepared as to remain suspended in the collodion. Then on pouring such a mixture over the plate the solvents would volatilise and leave the plate coated with silver haloid. As a consequence the bath would be entirely dispensed with, and the manipulations very considerably simplified.

Owing to the insolubility and colour of the silver haloids a liquid containing these in suspension has a milky appearance, and is consequently called an "emulsion," a word derived from the term used to denote certain pharmaceutical mixtures, containing oil and water, caused to coalesce by the addition of a third substance.

If collodion is the vehicle holding the silver haloid in suspension, we call the mixture a collodion emulsion; if gelatine has been employed, a gelatine emulsion.

To illustrate the preparation of an emulsion I have in this bottle an ounce of bromised collodion, containing 10 grains of zinc bromide, and to this I add 15 grains of silver nitrate, dissolved in two drachms of boiling alcohol, taking care to add the latter solution in small quantities at a time, and to shake well after each addition. Under these circumstances the mixture of silver bromide and iodide remains in suspension in the liquid, and adding a drop or two of strong nitric acid, I then pour the collodion emulsion over a glass plate in the usual way, and so obtain at one operation a film of pyroxyline containing the silver haloid.

In a second bottle I have an ounce of water in which 10 grains of zinc bromide has been dissolved, and adding to this 15 grains of silver nitrate dissolved in water you see the silver bromide formed by the interaction of the two solutions very soon settles to the bottom of the bottle as a flaky precipitate. The viscosity of the collodion prevents this settling down of the precipitated bromide, and so enables the milk-like emulsion to be readily prepared.



Instead of zinc bromide ammonium bromide might have been employed, and as illustrating the proportions found to answer in practice, the following formula \* for a collodio-bromide emulsion is appended:—

A.				
Pyroxyline	..	..	..	60 grains.
Ether	..	..	..	2½ ounces.
Alcohol	..	..	..	2½ „
B.				
Ammonium bromide	..	..	..	63 grains.
Water	..	..	..	60 minims.
Alcohol	..	..	..	½ ounce.
C.				
Silver nitrate	..	..	..	100 grains.
Water	..	..	..	60 minims.
Nitric acid	..	..	..	3 drops.

Representing the reaction of silver nitrate upon ammonium bromide as  $\text{AgNO}_3 + \text{NH}_4\text{I} = \text{AgI} + \text{NH}_4\text{NO}_3$ , we see that 170 parts by weight of the nitrate would suffice to combine with 145 parts by weight of the ammonium bromide. Consequently the 63 grains of ammonium bromide given in the formula would theoretically require only  $\frac{170 \times 63}{145} = 73\frac{25}{29}$  grains of silver nitrate, whilst 100 grains are actually used. We have therefore an excess of silver nitrate, the object of which will be apparent as we proceed.

This excess being, as we shall learn subsequently, removed, it might seem that the plates would require a preservative, but practically it is found that so long as the emulsion is made in presence of an excess of silver nitrate, no preservative is required.

Instead of operating as I have just done, I might have placed the collodion in a dish until the film had set, and then immersed the porous and still moist pyroxyline in a solution of silver nitrate until the soluble haloids had been completely converted into silver haloids. A thorough washing to get rid of the excess of silver nitrate would follow, after which the "pellicle," as the resulting solid is called, could be dried and re-dissolved in ether-alcohol; or I might have made the emulsion as in the first instance, and then placed the whole in a dish until it had set. When this occurred I could have washed it to remove the excess of silver nitrate, and re-dissolve the pellicle when dry in the ether-alcohol.

The second process is seldom used now-a-days, as for obvious reasons the first or third are preferable.

As regards the remaining two processes, it may be said that one yields as good a final result as the other, but the first is more convenient for preparing plates on a small scale, whilst the second is more suited to commercial operations.

\* Leaper, "Materi Photographica," page 193.

If, instead of using cold water for washing out the excess of silver nitrate, boiling water had been employed, then the emulsion would be rendered more sensitive.

It is, in fact, possible, as Abney\* has shown, to prepare a collo-bromide emulsion sensitive to the infra red by placing the emulsion prepared in the ordinary way in a retort immersed in boiling water until most of the ether-alcohol has evaporated, and then redissolving the dried pellicle in the usual mixture. It would be impossible to prepare an emulsion more sensitive than this by any other method, and this effectually disposes of the statement frequently made that gelatine emulsions are from ten to 100 times more sensitive than collodion emulsions. The fact is that very sensitive collodion emulsions being more difficult to prepare and costly, are less frequently met with than gelatine emulsions of equal sensitiveness.

Increased sensitiveness can also be obtained by permitting the emulsion to "ripen," which means leaving the materials in contact with each other for some time before proceeding to coat the plates.

The greater the quantity of silver nitrate used in the emulsion the sooner will it "ripen," or attain its maximum sensitiveness.

The action of heat in increasing the sensitiveness of silver bromide has already been explained. The efficacy of the "ripening" process depends, doubtless, upon the fact that silver bromide is soluble to a certain extent in silver nitrate.

To illustrate this point I add a drop of a weak solution of potassium bromide to a strong solution of silver nitrate, and as you observe no precipitate is formed, but on diluting the liquid with water the silver bromide is precipitated.

Now, it is well-known that silver bromide, in its most sensitive condition is composed of particles considerably larger than those constituting the other less sensitive allotropes. Thus †Eder has shown that in a particular instance the particles of silver bromide increased from  $\cdot 000031496$  inches to  $\cdot 00011811$  inches, the increase in size being accompanied by increased sensitiveness.

The presence of an excess of silver nitrate probably facilitates the change in the same way that the presence of a solution of, say, common alum, will cause a crystal of alum to grow.

In this beaker, containing a saturated solution of alum, there was placed a week ago a very small crystal of the small substance, and you perceive that this crystal has now attained respectable dimensions, and will continue to grow, in fact, so long as it remains in the solution.

You will understand, therefore, that the trace of silver bromide dissolved out by the silver nitrate will deposit silver bromide upon each particle of that substance in the film, and these particles increasing in this way in size, and being in consequence converted into more sensitive allotropes, will give a very rapid plate.

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\* Phil. Trans., 1880, p. 653, and 1886, Part 2, p. 457.

† "Modern Dry Plates," page 13.

It follows from this, that an emulsion prepared by mixing silver nitrate with collodion cannot be kept for an indefinite time without decomposition, but if the same emulsion is washed, and then redissolved, it may be preserved without alteration.

It has been found that, if the quantity of silver nitrate exceeds a certain limit, the emulsion fogs without exposure to light at all; a fact which we can readily explain by saying that the excess of silver nitrate produces the red-sensitive allotrope of silver bromide; but it is also known that the addition of aqua regia, or of chlorine water, to a foggy emulsion will restore it to its original condition, the action of these substances doubtless depending upon the fact that chlorine will decompose any allotrope of silver bromide into comparatively insensitive silver chloride with the simultaneous liberation of bromine.

If, again, the bromide used is, as is frequently the case, contaminated with traces of oxide, the presence of this compound will result in the production of silver oxide, itself fogging under a developer without previous exposure to light.

This silver oxide most oxidising agents would decompose, and it is to avoid the chance of fog, due to the presence of this impurity, that a little nitric acid is generally added to the emulsion: immediately emulsification is complete.

We have already learnt that the various allotropes of silver bromide reflect and transmit light differently, and practical use is made of this fact in ascertaining if the emulsion has ripened sufficiently and yet not too much. According to Warnerke,\* the emulsion is ready for use when a thin film of it spread on glass transmits orange-red light and reflects blueish-white light.

The fact that potassium iodide renders a collodion emulsion almost completely insensitive makes it possible to carry on the greater number of the operations by candle or lamplight. To illustrate this I expose this collodion emulsion plate to the light from burning magnesium, and then make a mark across on it with a strong solution of potassium iodide, when, as you see, the cross develops up lighter than the ground.

In fact, the operations I have described might be carried on by lamplight provided care was taken to immerse the plates or the emulsion in potassium iodide and to wash this off in the dark-room, and instead of potassium iodide, potassium bichromate or nitric acid might be employed instead and would be equally efficient, all of which substances probably act upon the allotropic silver bromide and cause it to revert to its more stable condition, with, perhaps, the simultaneous decomposition of a portion of it.

The quality of the pyroxyline exerts a great influence on the emulsion, and, as a general rule, it may be stated that the pyroxyline should be prepared so as to give as powdery a film as is consistent with the absence of structure in it.

You remember, of course, that the portion of the spectrum to

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\* "Bulletin de l'Association Belge de Photographie," IV., 35.

which silver bromide is sensitive differs from that affecting silver iodide, and you would in consequence be prepared for the statement that an emulsion containing silver bromide only behaves in a different way to one containing a mixture of iodide and bromide.

A general statement it may be taken that by adding silver iodide to an emulsion we diminish the sensitiveness of the plate to the red. By adding, in fact, sufficient iodide, say 20 per cent. or so, the plate behaves in the spectrum as if iodide only was present. It follows from this that the presence of a little iodide in an emulsion is advisable, at all events when excessive sensitiveness is not aimed at, for by using some of this substance the chances of fog by over-ripening or by the action of the non-actinic light used are reduced to a minimum.

The precise soluble bromide employed in the collodion might, at first sight, appear to exert little or no influence on the final result provided, of course, that the bromide is sufficiently soluble in alcohol-ether, but in practice it has been found that such is not the case. Warnerke\* has made a series of elaborate experiments upon this point, and classifies the bromides in the following way, those coming last on the list giving silver bromide, having to the least degree the qualities mentioned under the various headings:—

*Sensitiveness to white light.*—Zn, Cd, Na,  $\text{NH}_4$ , K.

*Sensitiveness to yellow light.*—Zn, K,  $\text{NH}_4$ .

*Sensitiveness to heat.*—Zn,  $\text{NH}_4$ , Na, K,

*Tendency to fog.*—Cd, Na,  $\text{NH}_4$ .

*Density giving power.*—Zn,  $\text{NH}_4$ , Cd, K.

The time required for the emulsion to ripen has been investigated by Stuart Wortley,† to whom the following table is due:—

Cd Br <sub>2</sub>	..	..	..	..	..	9 hours.
Zn Br <sub>2</sub>	..	..	..	..	..	10½ "
K Br <sub>2</sub>	..	..	..	..	..	14 "
Na Br	..	..	..	..	..	15½ "
$\text{NH}_4$ Br	..	..	..	..	..	17½ "

The reason of the variations indicated in the above tables has not yet been satisfactorily explained.

#### SUMMARY.

A photographic emulsion may be defined as a viscous liquid holding a finely divided silver haloid in suspension.

Silver bromide is more readily emulsified than silver iodide.

An emulsion prepared with an excess of silver nitrate is more sensitive than one prepared with an excess of soluble haloid.

Silver bromide is soluble in silver nitrate, the presence of which consequently facilitates the allotropation of the silver haloid.

Heat brings about a similar change. By long continued digestion at a high temperature a collodion emulsion can be prepared sensitive to the infra red.

\* † "B.J. of Photography," 1876.



An emulsion containing free silver nitrate if kept too long, fogs on development.

Potassium iodide, chlorine, nitric acid, &c., restore a foggy emulsion to its original condition.

An emulsion free from silver nitrate can be kept for long periods without change.

Silver bromide in its most sensitive condition consists of relatively large particles.

The addition of a little iodide to the soluble bromide used in the colour decreases the sensitiveness of the emulsion to the red, and makes it less liable to fog.

Different soluble bromides act in different ways as regards sensitiveness, period of ripening, &c.



## LECTURE XXII.

GELATINO-BROMIDE EMULSIONS—METHODS OF PREPARING SAME—  
NECESSITY FOR AN EXCESS OF SOLUBLE BROMIDE—USES OF  
IODIDES AND CHLORIDES—EFFECT OF HEAT AND OF AMMONIA IN  
PRODUCING SENSITIVENESS—MANUFACTURE OF EMULSIONS IN  
ACTINIC LIGHT—EXPLANATION OF THE ACTION OF GELATINE IN  
PRODUCING INCREASED SENSITIVENESS TO LIGHT—DIFFICULTY OF  
COATING GLASS PLATES WITH GELATINE EMULSIONS—NECESSITY  
FOR A SUBSTRATUM.

IN making collodion emulsion we dissolve, as you remember, the soluble bromide in the collodion, and add the silver nitrate to the liquid, purposely keeping the latter in excess.

If, instead of employing collodion, an aqueous solution of gelatine was used, the viscous liquid would again prevent the silver bromide from settling to the bottom, and we should have a gelatino-bromide emulsion.

To illustrate this I have here two flasks, each containing ten grains of potassium bromide dissolved in an ounce of water, but one of them contains, in addition, five grains of gelatine in solution. Adding to each of these flasks a drachm of a thirty-grain solution of silver nitrate, you see that the silver bromide rapidly settles in the one case to the bottom of the liquid, whilst in the other case it remains in suspension in it.

The following formula\* will sufficiently illustrate the essential difference between collodion and gelatine emulsions :—

A.					
Silver nitrate	..	..	..	..	40 grains.
Water	..	..	..	..	8 ounces.
B.					
Ammonium bromide	..	..	..	..	220 grains.
Ammonium iodide	..	..	..	..	15 „
Ammonium chloride	..	..	..	..	15 „
Nelson's No. 1 gelatine	..	..	..	..	80 „
Water	..	..	..	..	8 ounces.
Hydrobromic acid	..	..	..	..	quant. suff.
C.					
Nelson's emulsion gelatine	..	..	..	..	450 grains.

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\* Leaper, "Materia Photographica," p. 194

To prepare the emulsion I have in the upper vessel (fig. 58) the requisite quantity of silver nitrate, and in the lower one the soluble bromides, etc. Turning on the stopcock, I cause the contents of the upper vessel to be transferred to the lower one in a slender stream, keeping the mixture agitated during the whole time with a glass rod.

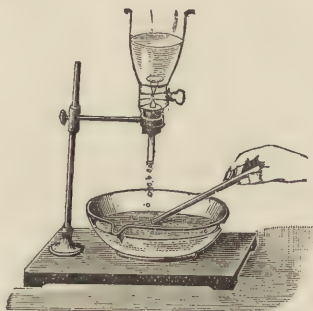


FIG. 58.—PREPARATION OF GELATINO-BROMIDE EMULSION.

Now pouring the emulsion into this shallow dish, I put it by in the dark for a short time until the gelatine has set, and will make further use of it when that has occurred.

We have already learnt that 170 parts by weight of silver nitrate interact with 145 parts by weight of ammonium bromide, therefore the 220 grains of ammonium bromide would require  $\frac{170 \times 220}{145}$  = 258 grains (nearly) of silver nitrate, whilst we have actually employed only 40 grains.

In this emulsion we have, then, a large excess of soluble bromide, whilst in the collodion emulsion we had an excess of silver nitrate.

What is the object of this excess of bromide? You remember that gelatine gives, with silver nitrate, a precipitate, meaning that some constituent of the gelatine has combined with the silver nitrate.

Now this compound fogs on the application of a developer, to illustrate which point I have here a piece of paper coated with gelatine, and, causing the red light to be turned on, I mark a cross upon it with a solution of silver nitrate, then washing off the excess of silver nitrate from the paper I place it in an alkaline developer, when, as you see, we obtain a black cross on a white ground.

I will now repeat the experiment in a slightly modified form. I this time float a sheet of paper coated with gelatine on a solution of silver nitrate, and having then washed off the excess, I mark a

cross upon the paper with a solution of potassium bromide. Again washing the paper I place the whole in the same developer as before, when, as you see, the cross comes out white on a dark ground. The potassium bromide has, in fact, converted the unstable gelatino-nitrate of silver (as we might call it) into comparatively stable silver bromide.

I can illustrate the same fact in another way. To this strong solution of gelatine in water I add a little silver nitrate, and so obtain the precipitate of silver gelatino-nitrate. Now adding to the mixture some solution of potassium bromide you observe that the gelatinous organic silver compound is at once converted into the characteristic flocculent silver bromide.

Since pyroxyline does not form with silver nitrate any compound which fogs without exposure to light, we may use an excess of nitrate in collodion emulsions, but when gelatine is employed we must, on the contrary, employ an excess of soluble bromide to prevent the formation of the objectionable silver gelatino-nitrate.

In a collodion emulsion we learnt that the presence of an excess of silver nitrate is essential if sensitiveness is aimed at, and it would seem to follow from this that a gelatino-bromide emulsion would be less sensitive than a collodio-bromide one.

We remember that the gain in sensitiveness of a collodion emulsion during the process of ripening was due to the fact that silver bromide is soluble to a certain extent in silver nitrate. Now silver bromide is also soluble in potassium bromide, to illustrate which fact I add a drop of a weak solution of silver nitrate to a strong solution of potassium bromide, when you see that no precipitate is formed, but on considerably diluting the mixture the resultant turbidity shows us that the silver bromide is held in solution only on condition that the solution of potassium bromide is sufficiently concentrated.

It would seem from this that a gelatino-bromide emulsion could be made sensitive by permitting it to ripen, and this would no doubt be the case were it not for the fact that gelatine maintained liquid for any length of time decomposes and yields products which react upon the silver bromide and cause it to fog on the application of a developer. What is the nature of these products of decomposition?

Heating a little dry gelatine in a tube with some lime and holding over the mouth of the tube some red litmus paper, you perceive that the red colour of the paper is changed to blue. Holding another piece of paper over a bottle of ammonia we obtain a similar result, and learn from the experiment that gelatine heated with lime gives off ammonia gas, a result due to the nitrogen which the gelatine contains.

A similar change takes place when gelatine is permitted to remain wet for a long time, and ammonia is, as we shall subsequently learn, a powerful means of converting ordinary silver bromide into its red sensitive allotrope.

Hence the ripening process which answers admirably with collodion does not answer with gelatine, owing to the partial decomposition of the gelatine. It is found, however, that sensitiveness may be obtained in two other ways. To illustrate the first method I again add a drop of a weak solution of silver nitrate to a strong solution of potassium bromide, and then boil the liquid, when you observe that the solution, clear at first, becomes gradually turbid. Now, you can readily understand that if we heated an emulsion of silver gelatino-bromide, the silver bromide dissolved in the first instance by the excess of soluble bromide thrown out of solution by the rise in temperature would serve here the same purpose as it did in collodion—it would increase the size of the particles of silver bromide first precipitated, which really means that it would convert the comparatively insensitive silver bromide first thrown down into a more sensitive allotropic modification. The change in size is accompanied, as you remember, by a change in colour, and this change I can easily demonstrate to you.

Adding some silver nitrate to the mixture of gelatine and potassium bromide contained in this tube, I obtain an emulsion of silver bromide in its least sensitive condition. Dividing this emulsion into two portions, I coat a glass plate with one of these, and, having boiled the other portion for a few minutes over the Bunsen burner, I coat a second glass plate with it. Now, passing both plates through the lantern, you perceive that one transmits orange and the other blue light.

The colour, by transmitted light, of a thin film of the emulsion spread over glass is, in fact, a practical means of judging of the amount of sensitiveness which the emulsion possesses at different stages.

To produce a sensitive gelatino-bromide emulsion we must then heat the silver bromide in contact with an excess of gelatine and of potassium or ammonium bromide, judging of the extent to which the allotropation of the silver bromide has proceeded by the examination, from time to time, by transmitted light, of a thin film of the emulsion spread upon glass. Evidently we must not carry the change too far, for if we do we should obtain a product which fogs without exposure to light at all, the silver bromide having in that case become converted into its red sensitive modification.

You will observe in the formula that a certain weight of gelatine is given by itself. What is the meaning of this? Gelatine by prolonged heating loses to a certain extent its power of setting, and as upon this property much of its value depends in practice, the emulsification of the silver bromide and its subsequent allotropation is affected in presence of a small portion only of gelatine. When the change is complete the liquid is poured over the remainder of the gelatine, and when this has swelled the whole is then remelted. By so doing any chance of the gelatine losing its power of setting is reduced to a minimum.

Our emulsion when brought to the required degree of sensitive-



ness contains an excess of soluble bromide and the soluble nitrates resulting from the decomposition by the silver nitrate of a portion of the soluble bromide used.

If we coated plates with it in that condition and permitted the emulsion to dry, these salts would crystallise out and spoil the film. We could of course get rid of them by washing the plates after coating, but a far better plan would be to permit the entire mass of the emulsion to stiffen and then break it up into small portions and wash these in water. The gelatine being more or less porous, would permit the water to permeate it and so dissolve out anything soluble, whilst of course, the insoluble silver haloids would remain behind.

You will observe that a certain quantity of hydrobromic acid enters into the formula. Its use is to convert any oxide present as impurity in the soluble bromide into silver bromide, and so prevent the emulsion from being foggy. In practice, the mixtures A and B are emulsified, and sufficient hydrobromic acid then added to give the solution a reaction distinctly acid to blue litmus paper.

The formula also contains some iodide and chloride. The use of the iodide is to enable the mixture to be boiled for a longer time without producing a foggy emulsion, and tends also to give greater density, and to enable more light to be used in the manufacture and subsequent development of the plates without and chance of fog. The addition of a little soluble chloride appears to accelerate development somewhat, and is for that reason very generally adopted, silver chloride being, in fact, more readily acted upon by an alkaline developer than either silver bromide or iodide.

We can now conveniently revert to the dish of emulsion which you remember we put by to set, but which has still to be washey free from everything soluble. Removing the emulsion from the dish with a glass spatula (fig. 59) I then break it up into small

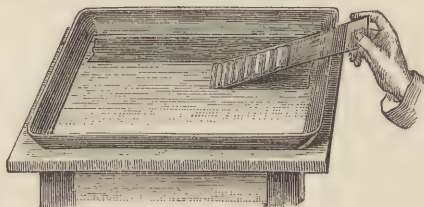


FIG. 59.—BREAKING UP THE EMULSION PRIOR TO WASHING.

portions and place these in a covered vessel under running water for at least three hours. At the expiration of that time it would be merely necessary to drain and partially dry the emulsion, then remelt it, pour it over the remainder of the gelatine previously



swelled in water, remelt the whole, filter and proceed at once to coat the plates.

Another method of producing sensitiveness is to employ ammonia. To illustrate this I mix solutions of silver nitrate and potassium bromide, sufficiently dilute to give only a slight precipitate of silver bromide, and then add ammonia to the whole, when, as you see, the precipitate dissolves.

Dividing now the liquid into two portions, I dilute one half with water, and boil the other half, when, as you see, turbid solutions result in both cases.

Silver bromide is, in fact, soluble in ammonia, and is reprecipitated on diluting, or on heating the mixture. You will readily understand, therefore, that if in the first instance I had added sufficient ammonia to the silver nitrate to redissolve the precipitate first formed, and then used that solution instead of plain silver nitrate, I should have obtained a more sensitive emulsion, and that emulsion could now be made very sensitive by boiling it for a much shorter time than if no ammonia was present. In this connection you will do well to remember the experiment I previously made of heating gelatine with lime.

The presence of the gelatine surrounding the particles of silver bromide no doubt increases the sensitiveness of the latter, but you must not look upon this increased sensitiveness as due to the absorption of bromine by the gelatine.

Gelatine possesses, in fact, practically no power of absorbing bromine, but liberates ammonia when light acts upon it, and this is probably the reason of its action as a sensitiser. To illustrate this I place some gelatine in the water contained in each of these tubes, and covering one tube with this black cloth, I expose the other for five minutes in front of the magnesium lamp. Now adding some Nessler's solution to each of the tubes we obtain no precipitate in that one which has remained in the dark, but a distinct precipitate in the other, which precipitate chemists well know indicates ammonia. Now you remember how ammonia facilitates the allotropation of the silver bromide in making the emulsion, and it is almost certain that the ammonia liberated during exposure to light acts in an analogous way.

In this connection I may mention that silver bromide in collodion precipitated in presence of an excess of soluble bromide takes longer to allotropise than silver bromide in gelatine, and since this proves that the gelatine facilitates the allotropation of the silver bromide by heat, which we know liberates ammonia from it, it is only reasonable to suppose that in a similar way it facilitates its allotropation by light.

It may be, perhaps, that the gelatine is itself sensitive to light and yields ammoniacal products which react upon the silver bromide, and, in view of the instability of gelatine, there is some reason for this assumption, which is also borne out by the well-known fact that the sensitiveness of dry plates is increased by

exposing them in contact with caustic potash or soda, substances which would facilitate the liberation of ammonia from the gelatine.

You will remember that when dealing with collo-emulsion I explained how the latter might be prepared by lamp-light. A similar method of procedure can be adopted when making gelatino-bromide emulsion, such as placing the emulsion in a strong solution of potassium bichromate, when any foggy products will be completely eliminated. It is only necessary to finally wash out the bichromate in non-actinic light.

With collodion no trouble is experienced in coating the plates, but it is far other with solutions of gelatine. Such solutions will not readily flow over a glass surface, with the result that it is difficult, if not impossible, to coat glass plates containing no substratum with a gelatine emulsion.

If, however, the glass receives a preliminary substratum of gelatine containing a little sodium silicate, then coating takes place with the greatest ease.

To illustrate this point, I have here two plates, one of plain glass, the other of glass coated with a substratum of gelatine and sodium silicate, and you observe that on pouring some gelatine emulsion over the first I cannot by any tilting force it to the edges, whilst over the other the emulsion flows as readily as collodion does over plain glass.

Since water evaporates less readily than ether-alcohol, a different method of procedure to that we adopted for collodion must be employed in coating plates with gelatine emulsion.

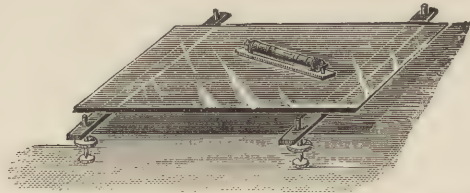


FIG. 60.—LEVELLED GLASS PLATE FOR USE IN EMULSION MAKING.

In this latter case the emulsion is poured over the glass in sufficient quantity to form, when dry, a film of a determinate thickness (about  $\frac{1}{2}$  ounce being taken for every 100 square inches), and the plate is then immediately placed on a levelled slab of slate or glass (fig. 60), and when the layer of emulsion has set, as it very soon does, the plates are then put into a drying closet (fig. 61), through which slightly warmed air circulates. Rapid drying is with gelatine an almost absolute necessity, owing to the fact that a moist film of it soon decomposes, and so produces fog.

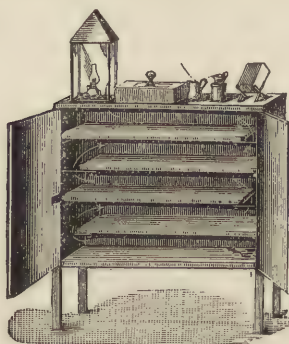


FIG. 61.—DRYING CLOSET FOR GELATINO-BROMIDE PLATES.

## SUMMARY.

A solution of *gelatine* in water being *viscous* prevents silver bromide precipitated in such a solution from *settling* to the bottom of the liquid.

*Silver nitrate* and *gelatine* give a product which *fogs* without exposure to light. This *fogging substance* is converted into silver bromide by a soluble bromide, say that of potassium or of ammonium.

*Gelatine* emulsions contain therefore an excess of soluble bromide.

Silver bromide is soluble in potassium bromide or in ammonia, and on boiling or on diluting the solutions the silver bromide is precipitated.

An excess of potassium bromide or the presence of ammonia in a gelatino-bromide emulsion facilitates the allotropation of the silver bromide.

*Gelatine* also facilitates this allotropation, probably by its tendency to give off ammoniacal products.

Long continued heating deprives *gelatine* of its power of setting.

A finished *gelatine* emulsion must be washed to remove the excess of soluble bromide, and the soluble nitrates formed by double decomposition.

*Gelatine* facilitates the action of light upon silver bromide.

Potassium dichromate prevents light from acting upon silver bromide.

A trace of sodium silicate enables glass plates to be coated with *gelatine* emulsion quite readily.

Plates coated with *gelatine* emulsion must be rapidly dried to prevent the decomposition of the moist *gelatine*.

## LECTURE

DIFFICULTY OF RENDERING COLOURS IN MONOCHROME ON ORDINARY PLATES—ORTHOCHROMATIC PLATES--USE OF COLOURED SCREENS—THEORY OF ACTION OF CERTAIN SUBSTANCES IN INCREASING SENSITIVENESS OF PLATES TO DIFFERENT RAYS—EDER'S RESEARCHES—SENSITISING PLATES BY MEANS OF ERYTHROSIN.

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AS a means of faithfully reproducing in black and white an engraving, &c., there is no fault to be found with photography, but it is far otherwise when the question is not to copy black and white, but to render in black and white objects which are themselves coloured.

Let us take the simplest case of the sort which could present itself, viz., the prismatic spectrum yielded by, say, the sun, and let us imagine that we were called upon to make a photograph which would truthfully render in black and white the visual intensities of the various spectrum colours.

Projecting the spectrum on the screen a cursory examination reveals at once the fact that the yellow is visually the brightest colour, and the violet the least bright. By photometric methods, which it would be foreign to my subject to describe, the visual intensities of different portions of the spectrum have been determined, and the curve V given in the frontispiece has been plotted from these determinations.

Now since the height of any point on that curve above the horizontal line gives the relative visual intensity at that point, it is clear that a perfect plate exposed in the spectrum should give on development quantities of silver at the various Fraunhofer lines corresponding to the heights of the various portions of the visual curve measured along those lines. Comparing the curve with I., II., III., we see that silver bromide gives the *nearest* approximation to this result, but an approximation which is still very far from the truth.

If we take, for instance (curve V), the visual intensity at D, and compare it with that at G, we see that the former intensity is about ten times the latter, whilst if we compare the opacity of the deposit on silver bromide (curve I) at these lines we see that the amount of silver at D is about  $\frac{1}{10}$  that at G.

Again, the visual effect ends at H, whilst the photographic plate registers almost as much again in the ultra-violet. It is quite evident, therefore, that even with silver bromide the effect given in black and white by a print made from a plate containing that substance and exposed in the spectrum would be a complete travesty of the effect as seen by the eye.



What holds good with the spectrum will hold good to a certain extent with all coloured objects, although, owing to the fact that most of these reflect a good deal of white light, we usually get a nearer approximation to truth than we would if no white light at all was reflected.

Here, for instance, is a piece of light yellow card on which a dark blue cross has been painted. Evidently the negative made from it should, to be true to nature, show a light cross on a dark ground, but passing the negative made on a commercial dry plate through the lantern, you see that it renders the whole in an exactly opposite way, viz., as a dark cross on a light ground.

An examination of curve I explains the reason. The dark blue cross reflects on the whole rays situated at the violet end of the spectrum, whilst the light yellow ground reflects on the whole rays situated at the other end, and since the former rays make a greater impression on the plate than the latter ones, we get the dark cross rendered by a comparatively dense deposit, and the lighter ground rendered by a less dense one, the relative densities being, of course, reversed in the print which I now show you, and in which you see we have a light cross on a darker ground.

This fact is well known to photographers, who express it by saying that blues photograph white, and reds black, the black and white referring here to the final result, *i.e.*, to the positive or print.

Comparing the two curves (I and V), it is evident that to cause the opacity of the deposit at various points of I to approximate more nearly to the corresponding opacities in V we must do two things, *i.e.*, diminish the sensitiveness of the plate for the violet end of the spectrum, and increase its sensitiveness for the red end.

Let us attack the first part of the problem. Red glass absorbs violet, but lets through red, in consequence of which fact we may, by interposing a piece of such glass in the path of the spectrum, very materially reduce the actinic intensity of the violet rays without *proportionately* decreasing the actinic intensity of the red. Here, for instance, I have a series of thin glass plates coated with a varnish slightly tinted with a red pigment. If I interpose one of these in the path of the spectrum the visual effect is practically the same as before, but the actinic effect is very different.

Causing the red light to be turned on I expose in the spectrum a slip of bromide paper, then develop it, and place the developed paper in the spectrum, when you see that the effect ends somewhat abruptly just beyond the visible violet. If I had used two plates instead of one I should have reduced the sensitiveness to the violet end still more, and so obtain a nearer proximation to what I want.

To illustrate the matter in another way, I project on the screen a negative of the dark blue cross on the light yellow ground made on an ordinary dry plate by interposing three pieces of lightly tinted yellow glass between the lens and the sensitive plate, and



you see that the deposit is of the same opacity throughout, the yellow glass having, in fact, so reduced the actinic effect of the blue rays reflected by the cross as to make the effect they exert equal to that of the rays reflected by the light yellow ground.

But this is not of course a solution of the problem, for we want, in addition to diminished sensitiveness to the violet end of the spectrum, increased sensitiveness to the red end, and this is what no tinted glass can give.

Fortunately, however, we have it in our power to get what we want in another way.

Before, however, describing how this result is arrived at, it will be necessary to briefly review some of the ground we have already traversed.

We have learnt that certain substances are sensitive to certain rays, precisely because these rays are absorbed by the molecules of the substances in question, and become converted in the molecule into work of some kind.

Taking, for instance, that allotrope of silver bromide which transmits red light, we found that it was comparatively insensitive to spectrum red, the allotrope most sensitive to the red end of the spectrum being that one which transmitted least red, *i.e.*, absorbed most of it, such an allotrope being capable, as you remember, of transmitting blue light.

We may in fact put the whole matter into one statement by saying that any silver haloid is most sensitive to those rays which it most energetically absorbs.

I can illustrate this fact in the following way:—On these two plates are films containing respectively silver bromide and precipitated chalk. To the unaided eye one appears as opaque as the other, and there is little to choose between them in the matter of colour.

Again, causing the red light to be turned on, I place the two films in contact with a sensitive plate, and having burnt an inch of magnesium in front of the whole I develop the plate, when, as you see, we get practically no effect on the portion of the plate beneath the silver haloid, whilst the portion beneath the chalk is marked by a dense deposit.

What we want, you remember, to cause the spectrum to be rendered truthfully in black and white is to increase the sensitiveness of the plate to the red.

Now, since this means causing it to absorb more red than before, it should be possible by staining the film itself to obtain just what we want. Here, for instance, is a plain gelatine film tinted with a little erythrosin, and placing it in the path of the spectrum you see that it absorbs the yellow and some of the green, and should consequently, when applied to a gelatino-bromide film, increase its sensitiveness for these colours.

To prove the fact, I have prepared a slip of bromide paper, the lower half of which has been painted over with a very dilute

solution ( $\frac{1}{10}$ th per cent.) of this substance, and this piece of paper I now expose in the spectrum and develop it, when, as you see, there is a marked difference between the two halves. The upper portion shows the visual effect of the spectrum upon silver bromide as curve I in frontispiece gives it, *i.e.*, the deposit is densest in the portion of the blue nearest the violet. In the lower half, on the other hand, we have a fairly dense deposit in the portion of the yellow nearest the green, showing that the erythrosin actually increased the sensitiveness at that spot. If, in fact, we exposed a glass plate coated with silver bromide and erythrosin in the spectrum, and having developed it, measured the opacity of the deposit at different portions, we should obtain a curve like IV in frontispiece—a curve which is, of course, a nearer approximation to V than I is.

But unfortunately, although we thus increase the sensitiveness of the plate for the red, we also increase its sensitiveness for the violet, and as a result we must use a plate of yellow glass between the lens and the sensitive surface.

To illustrate the effect in a particular case I project on the screen a negative of the dark blue cross on the light yellow ground taken on a plate dyed with erythrosin, and used without a screen, and you observe that there is little difference between the cross and the ground, the cross again coming out darker than the ground, although less dark than when an undyed plate was used, but now projecting another negative taken on a dyed plate used with a screen we have, as you see, at last obtained what is wanted, the cross now being markedly lighter than the ground.

Such plates are said to be ortho or isochromatic, terms denoting the fact that when properly used they are capable of rendering colours more truthfully in monochrome than ordinary plates can do.

You will, however, do well to bear in mind that such plates are by no means necessary in every case. For black, white, or grey, which we may look upon as a mixture of black and white, such plates possess no advantage whatever over ordinary ones.

If violets or blues are present as well, then the employment of a yellow screen at the nodal point of admission or emission of the lens will give us what we want. Assuming that a pure violet only is to be photographed with white, black and grey, then the lighter in tint that violet is, *i.e.*, the more white light it reflects, the less deeply tinted will our screen need to be.

If, on the contrary, the violet is, as we call it, a dark one, *i.e.*, reflects but little white light, then a more highly coloured screen must be employed to get a proper effect. It is, in fact, in the proper adjustment of the depth of colour of the screen to the depth of colour of the object photographed that the great difficulty lies.

If colours as we see them in nature reflected no white light, and were pure, very little trouble would be experienced, but as it is, we have to contend with not only the fact that the colours

themselves are not pure, but also the fact that they reflect more or less white light.

Let us suppose now that we had to photograph yellow and blue. Then it is clear that no screen could possibly enable the red to make a greater impression than the blue, but by using an orthochromatic plate, sensitive to red with a screen, we can tone down the exalted sensitiveness of the silver bromide for the blue to such a degree that the actual deposit, where red rays fell, would be greater than where blue rays acted. The great difficulty would here again lie in the proper adjustment of the depth of colour of the screen.

And it will be readily understood that if the object was to copy a painting in which we have, perhaps, every colour of the spectrum, and not one of them pure, the difficulty of the undertaking would become enormously increased.

To illustrate in another way the difficulties we have to deal with in work of this class, I may mention that Eder\* has shown that a plate capable of reproducing colours with their relative intensities, as seen by a normal eye, should present the following characteristics when exposed in the solar spectrum: The orange at C and the blue at F should be rendered as equally dense deposits, the yellow at D by a deposit six times as dense as this, the green at E by one three times as dense, and the end of the visible violet by one ten times less dense. To get this result should be, and is, the aim of orthochromatic photography, but you will readily understand that to obtain even an approximation to this result demands an operator possessing the highest technical training.

As regards the method of applying the dye, it may be stated that practically the same result is obtained whether the dye is mixed with the emulsion in the process of manufacture, or the plate merely dipped in a solution of the dye when finished.

You will remember that as a general rule the colours absorbed by a substance determine its effect when that substance is applied to a gelatino-bromide plate, but this is by no means invariably the case. Thus, the colouring matter of the sunflower decreases the sensitiveness of silver bromide for the red, and indigo, which absorbs the yellow, does not increase its sensitiveness for that colour. The most remarkable exception is, however, that afforded by salicine, a substance which, although perfectly colourless, increases the sensitiveness of silver bromide to the green and red.

The generally accepted explanation of the action of these substances in the manner indicated is that the substances themselves undergo decomposition in certain portions of the spectrum, and give rise to products which allotropise the silver bromide with which they are mixed. It is significant in this connection that the substances which have been found to be most efficient are substances which might by their decomposition give rise to alkaline products. Thus

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\* "La photographie des objets colorés avec leur valeur réelle."

eosin, rose bengal, and erythrosin contain potassium, and cyanin contains nitrogen. The former two might decompose into caustic potash and other products, the latter into ammonia and something else. The explanation just given is borne out by the fact that the addition of ammonia invariably increases the efficacy of the colouring matter.

#### SUMMARY.

Any silver haloid can give a true rendering of objects which are black, white or grey.

Ordinary silver bromide cannot truly render in monochrome coloured objects as seen by the eye.

A perfect plate should give a curve of sensitiveness identical with the curve of visual effect (Plate V., frontispiece).

Ordinary silver bromide is too sensitive to the violet end of the spectrum, and too insensitive to the red end.

A red or yellow screen used in front of a film of silver bromide diminishes its sensitiveness to the violet.

Certain dyes, such as erythrosin, increase the sensitiveness of silver bromide to the red.

A dyed plate used with a screen will approximately render the spectrum in black and white (so far as relative colour intensities go) as the eye sees it.

Orthochromatic photography has for object to render the photographic intensity at any part of the spectrum the same as the visual intensity at that part.

Any compound is most sensitive in the absence of secondary reactions to that spectrum colour which it absorbs.

Erythrosin probably acts by absorbing the red rays and being decomposed by them, liberating in the latter case certain products which allotropise silver bromide.



## LECTURE XXIV.

THE DEVELOPMENT OF THE INVISIBLE IMAGE—SUB-DIVISION OF PHOTOGRAPHIC DEVELOPERS INTO TWO CLASSES—ABSORPTION OF OXYGEN BY FERROUS SULPHATE AND POTASSIO-FERROUS OXALATE—ACTION OF SILVER NITRATE UPON THESE SUBSTANCES—ACTION OF ACIDS, ETC., IN RESTRAINING DEVELOPMENT—MECHANICAL EFFECT OF DIFFERENT SUBSTANCES UPON SLOWLY DEPOSITING METALLIC SILVER—ELECTRICAL ACTIONS GOING ON DURING DEVELOPMENT—EFFECT OF DILUTION AND OF RESTRAINERS IN MODIFYING DENSITIES OF VARIOUS PORTIONS OF DEPOSIT.

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TO make visible the effect produced by light on the surface of a sensitive film of silver haloid, we employ what is called in photographic parlance a developer. This is, broadly speaking, a substance which exerts an action upon those portions of the surface exposed to light different from that which it exerts upon the unexposed portions. It is, in fact, upon this difference in effect that the possibility of development depends.

We may conveniently sub-divide those developers employed with the silver haloids into two classes, viz., substances exerting a comparatively feeble reducing action, and containing free silver nitrate, and substances exerting an energetic reducing action, and containing no free silver nitrate. As an example of the first type of developer, we may take ferrous sulphate, acidified with acetic acid (which in actual use is mixed with a little silver nitrate), and as an example of the latter, potassio-ferrous oxalate, obtained by mixing solutions of potassium oxalate and ferrous sulphate.

A substance exerting a reducing action is one which absorbs oxygen, and I will begin by showing you the facility with which these two substances, ferrous sulphate and potassium ferrous oxalate, will respectively absorb this gas.

The glass tube is supported over metallic mercury (fig. 62) containing oxygen gas, and by means of the curved pipette I introduce into the tube a little ferrous sulphate, when you see that comparatively little absorption takes place. Now adding to this, by means of the pipette, some potassium oxalate solutions, I thereby convert the greenish ferrous sulphate into orange potassio-ferrous oxalate, and the rise of the liquid in the tube at once tells us that this substance absorbs oxygen much more energetically than the ferrous sulphate first used.

If again I place in two tubes some ferrous sulphate and potassium ferrous oxalate, and add to each a few drops of a one per cent. solution of silver nitrate, you see that metallic silver is at once thrown down in the tube containing the potassio-ferrous



oxalate, whilst the mixture in the other tube remains comparatively clear.

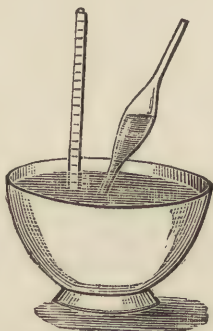


FIG. 62.—ABSORPTION OF OXYGEN BY POTASSIO-FERROUS OXALATE.

A wet collodion plate is, as you well know, exposed to light whilst its surface is wet with a solution of silver nitrate. If I took such a plate as it came from the dark slide after exposure and flooded its surface with potassio-ferrous oxalate, metallic silver would be precipitated all over the film, and no development of the image would be possible, but if I had used ferrous sulphate instead a gradual precipitation of the silver would occur, and for reasons that we shall learn in a moment the slowly depositing metallic silver would attach itself only to those portions of the film upon which light had acted.

The first point we must consider is the action of ferrous sulphate upon silver nitrate. If we mix these two solutions they interact in accordance with the equation

$6\text{FeSO}_4 + 6\text{AgNO}_3 = 2\text{Fe}_2(\text{SO}_4)_3 + \text{Fe}_2(\text{NO}_3)_6 + 3\text{Ag}_2$ ,  
the ferrous sulphate becoming converted into ferric sulphate and nitrate and metallic silver being precipitated.

If the solutions are concentrated the precipitation of metallic silver takes place at once; if they are dilute, or have been mixed with, say, acetic acid, the precipitation takes place in a more gradual manner.

To illustrate the action of the acetic acid I place in these two tubes equal quantities of ferrous sulphate solution, adding to one of the tubes ten drops of glacial acetic acid. Now letting fall into the unacidified ferrous sulphate a single drop of a ten per cent. solution of silver nitrate, you perceive that an immediate precipitate falls, whilst to the other tube I must add twenty drops of the silver nitrate before any metallic silver begins to be precipitated.

What is the action of the acetic acid in checking the precipita-

tion of the silver nitrate? The most probable explanation appears to be that the silver, in the act of being precipitated (nascent state), combines with the acetic acid to form silver acetate, so that the ferrous sulphate must decompose not only silver nitrate, but silver acetate as well, before any metallic silver can be precipitated. Instead of acetic acid, citric, nitric, or sulphuric acids might be used, and doubtless act in a similar way.

As an example of a developer containing ferrous sulphate the following formula is appended:—\*

Ferrous sulphate	..	..	..	1 oz.
Glacial acetic acid	..	..	..	1 "
Water	..	..	..	16 "
Alcohol	..	..	..	quant. suff.

In a developer of this class we have therefore a liquid capable of exerting a relatively feeble reducing action, and from which metallic silver is being slowly deposited.

In the case of a wet plate the silver itself is derived from the surface of the film moistened with that substance; in a dry plate developed in a similar way the silver nitrate must be added to the developer made up in accordance with the formula just given, otherwise no image will be obtained.

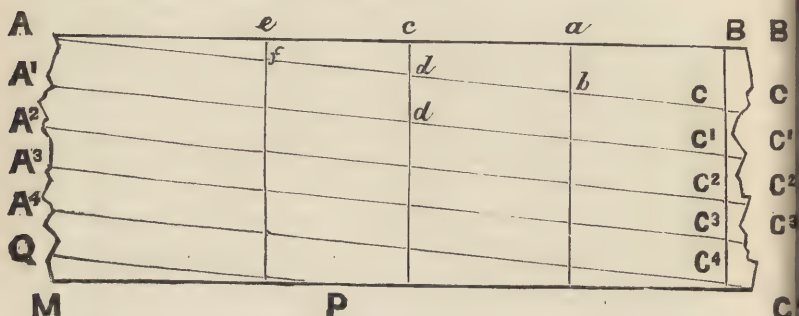


FIG. 63.—GRAPHICAL REPRESENTATION OF THE ACTION OF LIGHT UPON A FILM OF SILVER HALOID.

Let us suppose now that we took a rather long and narrow slip of glass, coated it with a film of silver iodide moistened with silver nitrate, and then exposed the whole to actinic light in such a way that upon development we should get great density at one end, gradually shading off into complete absence of deposit at the other. Then according to the principles which were laid down in former lectures we may look upon different portions of that film as con-

\* Leaper, "Materia Photographica," page 182

taining after exposure and before development different quantities of allotropic silver iodide.

Let A B in the figure represent the surface of the film, then after exposure we shall have at B a layer of allotropic molecules equal in depth to, say, B C, whilst at *a, c, e* the depth will only be *a b, c d, e f*, comparatively few molecules having been allotropised towards A.

I get a rough approximation to this state of things by exposing, as I am about to do, a film of silver iodide in front of the burning magnesium, whilst holding the glass plate in a very slanting direction.

Causing the red light to be turned on, I expose the film and then develop it, when on passing it through the lantern you perceive that the deposit is densest where the light acted most strongly, and feeblest where the light acted least strongly.

Clearly, therefore, the slowly depositing silver has somehow attached itself in greatest quantity to that portion of the plate where light exerted most effect.

If, now, I expose another plate beneath this black cross, and then develop it, you perceive that the deposit is densest where light has acted, no deposit being obtained where light has not acted. It is evident, therefore, that the slowly depositing silver begins by attaching itself to those portions of the plate which have been acted upon by light.

This initial action is commonly, for want of a better name described as mechanical, which is tantamount to saying that the slowly depositing silver does not in any way combine with the allotropic molecules. To illustrate this I have here a very carefully cleaned glass plate, and with a stick of paraffin I write the name of that substance upon it. Now placing the whole in acidified ferrous sulphate mixed with silver nitrate, you perceive that the glass plate itself gradually becomes coated with metallic silver, whilst the portions of it upon which the word paraffin has been written remains to the last quite free from deposit.

We get, in fact, in this way the word paraffin in clear glass on a slightly obscured ground.

Now, we may take it that neither the glass nor the paraffin exert any *chemical* effect upon the silver nitrate, and this being the case we explain the result by saying that the glass surface when clean *mechanically* causes the silver to be deposited upon it, rather than upon the thin layer of paraffin.

But our explanation is by no means complete, for as long as the film of silver iodide acted upon by light remains in the developer so long will it continue to gain in density.

To illustrate this point I place in this glass cell that portion of our long strip of glass which had been least acted upon by light, and pour over it a dilute acidified solution of ferrous sulphate mixed with a little silver nitrate, when, as you see by the image projected on the screen, the deposit continues to gain in density,

and this would continue for any length of time we please, provided the supply of silver nitrate and of ferrous sulphate was kept up.

It appears, in fact, as if a minute quantity of metallic silver acted as a nucleus for the deposition of a relatively enormous amount of the same metal.

What is the cause of this action? To answer this question, I have here a glass tube bent in the form of a V, and narrowed at the centre to very small dimensions. In one limb is a solution of ferrous sulphate, and in the other one of silver nitrate, the two solutions being prevented from mixing by a little solidified plaster of Paris placed in the narrowed portion. Dipping into the liquid in each limb is a silver wire, and connecting my galvanometer wires to the silver wires in the cell, the motion of the needle at once tells me that a current of electricity is passing.

Now it is well known that such a current can bring about the decomposition of a substance.

To illustrate this point I have in the glass cell in the lantern a solution of silver nitrate, and dipping into it these two silver wires, connected to the battery beneath the table, you see that upon one of them minute filaments of metallic silver at once appear.

The mixture of ferrous sulphate and silver nitrate would act in a precisely similar way, but would take rather longer to produce an equivalent effect. To show you, however, that such an effect will take place without the use of an extraneous source of electricity, I now place another cell in the lantern.

This contains in one half a strong solution of silver nitrate, and in the other half a solution of ammonio-sulphate of iron, the two liquids being prevented from mixing by a diaphragm of vegetable parchment. Dipping into the liquids is a bent silver wire, and to the portion of that wire in the silver nitrate you perceive that minute crystals of metallic silver have attached themselves.

In a developer containing ferrous sulphate and silver nitrate we have then two liquids which react upon each other, and yield an electric current, and if in such a liquid we place any substance which conducts electricity, upon that substance will metallic silver be slowly deposited.

The substance need not necessarily be metallic silver; any conductor of electricity will do. To illustrate this, I have here a perfectly clean glass plate, and with pieces of silver, tin, copper, and an ordinary blacklead pencil (carbon), I write the names of these substances on the glass. Now placing the plate in the developer contained in the glass cell in the lantern you perceive that the names of these substances, although at first almost invisible, are rendered more and more apparent, the slowly depositing metallic silver attaching itself to those portions of the glass which had been written upon.

Let us revert now to our strip of glass (fig. 64) exposed so as to have a comparatively large amount of allotropic silver iodide at B C, and little or none at A. Over the whole of that surface



metallic silver is first mechanically deposited, when the plate is plunged in the developer, most silver being deposited at B C and least at A, and this deposit of silver then acts towards the silver nitrate and ferrous sulphate in the developer just as the silver wire did in our cell, with the result that silver continues to be deposited over the surface so long as there is any silver nitrate to be decomposed and any ferrous sulphate to decompose it. Why *most* silver should at the start be mechanically deposited at B C requires no explanation, for it is self-evident that if the allotropic silver bromide causes silver to be mechanically thrown down upon it at all, the greater the depth of the layer of the allotropic substance the greater will be the amount of silver deposited upon it.

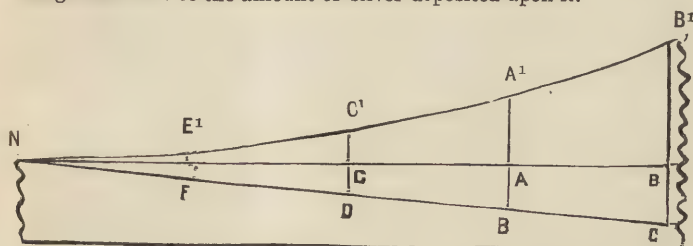


FIG. 64.—GRAPHICAL REPRESENTATION OF DEVELOPMENT BY SLOWLY PRECIPITATING SILVER.

We may, in fact, in our diagram look upon B C, A B, C D, E F and A as representing either varying thicknesses of allotropic silver bromide, and at the beginning of development varying thicknesses of mechanically deposited metallic silver.

Looking for the moment upon N B C as a series of short silver wires of gradually increasing thicknesses, the electrical conductivity at any point along it will be measured by the square of the diameter of the particular wire at that point. Calling the diameters at A, E, C, A, B, 0, 1, 2, 3, 4 respectively, then the conductivities will be 0, 1, 4, 9, 16.

Now since the amount of metal deposited by a current is proportional to that current, and since a current varies directly as the conductivity of the material through which it passes, the amount of metal deposited over A, E, C, A B will be given by lines in the proportion of 0, 1, 4, 9, 16. We shall then have metallic silver deposited in amount proportionate to the curve shown in fig. 64.

But we must clearly bear in mind that the curve N B¹ B has reference merely to the silver electrolytically deposited over the silver mechanically thrown down at N B C. If the developer acts for a longer period, then we shall have to consider the lines E¹ F, C¹ G, A¹ B, B¹ C, the amount of metal now deposited being propor-

tional to the squares of these new lines. In consequence of this the longer development takes, or what amounts to the same thing, the more dilute or the more acid we make the developer, the greater will be the amount of contrast, as we put it photographically, between the deposits at N and B<sup>1</sup>.

It will be at once inferred, from all this, that the material of the image on a plate, developed with acidified ferrous sulphate and silver nitrate, is derived, not from the film itself, but from matters extraneous to it.

To illustrate this point I have here a dry collodion plate prepared with coffee in the manner indicated on page 159, and exposed beneath a negative. Washing off the preservative with a little warm water, I plunge the plate into acidified ferrous sulphate, but no trace of an image appears. Pouring back the developer into the measure, I add to it a few drops of a dilute solution of silver nitrate, and reapply the whole to the plate, when the image makes its appearance and develops up to full intensity.

In this kind of development again the image must be *on* the surface, and not beneath it. That this is actually the case admits of very ready proof. I have merely to place the plate just developed into dilute nitric acid, when every trace of the image disappears, and the most careful scrutiny, even under the microscope, fails to reveal any irregularities in its surface, such as would have occurred had the material of the film itself been dissolved away.

The plate is now, in fact, in exactly its original state, and to prove this I wash it free from nitric acid, moisten the surface with a solution of silver nitrate, expose it beneath this black cross, and reapply the developer, when, as you see, the cross comes out white on a black ground, exactly as it would if the plate had not been used before at all.

You will observe that the developer contains alcohol. The object of this is purely mechanical, and the addition is really unnecessary if the silver bath is new, or if the plate to be developed is a *dry* one. Usually, however, the bath contains alcohol and ether, and these substances present on the film just as the developer is being applied to it would prevent the even action of the latter if it was made up with water only. To avoid this some alcohol is mixed with the ferrous sulphate to enable the developer to act more regularly upon it.

Silver iodide has been taken as a typical haloid in the method of development just considered; but it must not be inferred from this that it is the only haloid which admits of being developed in this manner, for, as a matter of fact, silver bromide and chloride behave after exposure to light in practically the same way when placed in an acidified solution of ferrous sulphate mixed with silver nitrate.

#### SUMMARY.

*Ferrous sulphate, particularly if acidified, is a feeble oxygen absorbent. Potassio-ferrous oxalate is an exceedingly energetic one.*

*Potassio-ferrous oxalate immediately decomposes silver nitrate. Acidified ferrous sulphate decomposes it slowly.*

*Slowly-depositing metallic silver is mechanically precipitated over silver iodide upon which light has acted.*

*Ferrous sulphate and silver nitrate react upon each other, producing an electric current, which can itself cause silver nitrate to be precipitated from its solutions. The more powerful an electric current is, the greater the amount of silver which it will precipitate in a given time.*

*The varying densities obtained on developing silver iodide exposed to light of varying intensities are due to the varying conductivities of the varying amounts of silver precipitated on and in the film.*

*The longer the development takes, i.e., the more dilute the developer, or the more highly restrained it is, the greater the contrast.*

*Acetic or other acids act as restrainers by combining with the nascent silver.*

*A typical wet plate developer contains silver nitrate, ferrous sulphate, and acetic acid.*

*The deposited silver constituting a negative developed with such a developer is on the film, not in it.*

## LECTURE XXV.

STAINING OF GELATINE BY SILVER NITRATE—EMPLOYMENT OF RELATIVELY POWERFUL REDUCING AGENTS TO DEVELOP EMULSIONS CONTAINING THE SILVER HALOIDS—ACTION OF POTASSIO-FERROUS OXALATE UPON A FILM OF SILVER BROMIDE SUPERFICALLY CHANGED BY EXPOSURE TO LIGHT—THEORY OF SO-CALLED ALKALINE DEVELOPMENT—ACTION OF ACCELERATORS AND RESTRAINERS.

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IT has been already pointed out to you in a previous lecture that silver nitrate precipitates gelatine, and for this reason if a developer containing silver nitrate was applied to a dry plate containing a silver haloid, mixed with gelatine, this latter substance would become badly stained.

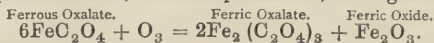
It is only, in fact, when the vehicle containing the silver haloid is pyroxyline that the method of development described in the last lecture is practically applicable. To illustrate this, I have here an ordinary commercial gelatine dry plate, containing silver iodide and bromide, and exposing it to actinic light beneath this black cross, I then place it in a mixture of acidified ferrous sulphate and silver nitrate, when, as you see, the cross develops up, but the whole surface of the film is at the same time badly stained.

Fortunately, however, there exists another method of developing such plates without the slightest risk of staining them.

Exposing a second plate beneath the black cross, I then place it in a solution of potassio-ferrous oxalate containing no free silver nitrate, and now, as you see, we get a result quite free from every trace of stain.

You remember, of course, that this solution of potassio-ferrous oxalate is a far more energetic oxygen absorbent than acidified ferrous sulphate, and it is, in fact, upon its power of rapidly deoxidising most substances with which it comes in contact that its value as a developer depends.

We must first of all consider what happens when the potassio-ferrous oxalate absorbs oxygen. This substance really owes its efficacy to the ferrous oxalate entering into its composition, and this ferrous oxalate becomes converted into ferric oxalate in contact with a substance containing a store of oxygen in accordance with an equation which, in its simplest form, we might write thus—



If an acid is present as well, then the ferric oxide will become converted into a salt of that acid.



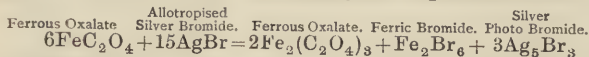
Now, in a film of silver bromide which has been exposed for a short time to actinic light, we have on the surface a number of allotropised molecules similar in kind, as you remember, to those present in red sensitive bromide emulsion prepared in non-actinic light.

What is the action of the ferrous oxalate upon these molecules? You remember, of course, that a prolonged exposure to light converts these molecules into silver photo bromide, which we have represented provisionally as  $\text{Ag}_5\text{Br}_3$ .

Now it is exceedingly probable that the initial action of the developer consists in effecting an identical change. We know that silver bromide tends to liberate bromine, and that ferrous oxalate tends to absorb it, and if we put these two things in contact, even in non-actinic light, the ferrous oxalate will become oxidised and the silver bromide converted into what is probably silver photo bromide.

If, however, we give the silver bromide a short exposure to light, then we make it to absorb a certain amount of energy, and less energy will now be required (supplied in the form of a solution having a tendency to oxidise) to cause bromine to be liberated from it.

We may, then, fairly assume that the initial action of the developer consists in splitting up the surface molecules of allotropised silver bromide into silver photo bromide and bromine, which latter then oxidises the ferrous oxalate into ferric oxalate. According to this view the initial change might be represented thus—



This, however, by no means represents the whole change, for it is well known that density can be obtained by leaving the exposed plate for a longer time in the developer, so that these surface molecules of silver photo bromide must in some way be capable of acting upon the unaltered molecules of silver bromide immediately beneath them.

Before attempting to explain the next series of changes it may be well to practically illustrate the fact that density continues to increase so long as the plate is left in the developer.

To illustrate this point, I give this plate a short exposure to light, and my assistant will then cut it up into six pieces, and place each piece for 1, 2, 3, 4, 5, and 6 minutes respectively in the developer, when we shall find that the piece longest in the developer will possess the greatest density.

As to the nature of the final deposit obtained, *i.e.*, the developed image itself, this can be proved in the most conclusive manner to consist for the most part of metallic silver.

To prove this point I place this portion of a fully developed plate in nitric acid, when you see it dissolves, leaving only a faint residue, and the solution so obtained gives the usual white precipitate on adding to it a solution of hydrochloric acid.

It is evident from all this that in the first place the metallic silver constituting the developed image was obtained from the silver bromide of the film itself, and in the second place, that the reaction previously given does not represent the whole change, for if it did the developed deposit should be insoluble in nitric acid. To illustrate the matter in another way, I have here a bottle of collodio-bromide emulsion, and exposing to actinic light a glass plate, one half of which has been coated with gelatino-bromide emulsion, I pour over the plain glass and over a portion of the exposed film some of the collodio-bromide emulsion. After the ether-alcohol has evaporated, I place the entire plate in the potassio-ferrous oxalate developer and obtain, as you see, the following result:—The collodio-bromide on the plain glass has not blackened at all, whilst that over the exposed layer of silver bromide has blackened. In fact at the latter portion of the plate we have greater density than where only gelatine and silver bromide were present, and this shows that in some way the product yielded by the developer acting upon the exposed silver bromide has acted upon the same substance not exposed to light at all in such a way as to enable the developer to darken it.

Now, what are the substances in intimate contact with each other in this case? Firstly, the developer itself, which we may look upon as a bromine absorbent (this being tantamount to saying that it tends to become oxidised); secondly, the product of its action upon the molecules acted upon by light, which product, we have good reason to believe, is silver photo bromide; and thirdly, the molecules of unaltered silver bromide above and below this.

Now we have already seen that a substance in the nascent state possesses exalted affinities, and the silver photo bromide is actually in this state. What is more reasonable to suppose than that this silver photo bromide acts upon the unaltered silver bromide thus— $\text{Ag}_5\text{Br}_3 + 2\text{AgBr} = 5\text{AgBr} + \text{Ag}_2$ , the silver photo bromide becoming, in fact, reconverted into silver bromide with the simultaneous splitting up of the molecules immediately beneath and above it into metallic silver.

We have now two things to consider, viz., the five molecules of silver bromide and the single molecules of free silver. As regards the former the silver bromide being also in the nascent state is probably spilt up by the developer into silver and bromine, the latter serving to oxidise more ferrous oxalate, the free silver separated forming the beginning of the deposit. As regards the single molecule of free silver produced by the action of the silver photo-bromide upon the silver bromide, it also being in the nascent state reacts upon the molecules of silver bromide immediately beneath it, converting them into silver photo-bromide, thus— $\text{Ag}_2 + 3\text{AgBr} = \text{Ag}_5\text{Br}_3$ , which latter substance then again reacts upon more silver bromide in the manner just indicated, the change continuing until the bottom of the film is reached. When this occurs we should have on the plate metallic silver plus a small

quantity of silver photo-bromide, the presence of the latter accounting for the fact that the developed deposit does not wholly dissolve in nitric acid.

Grouping all these facts together we may represent the succession of changes in the following way:—

1. Action of short exposure to actinic light. Allotropation of AgBr molecules.

2. Initial action of developer upon these allotropic molecules  $6\text{FeC}_2\text{O}_4 + 15\text{AgBr} = 2\text{Fe}_2(\text{C}_2\text{O}_4)_3 + \text{Fe}_2\text{Br}_6 + 3\text{Ag}_5\text{Br}_3$ .

3. Action of nascent silver photo-bromide upon subjacent molecules of unaltered silver bromide— $6\text{Ag}_5\text{Br}_3 + 12\text{AgBr} = 30\text{AgBr} + 6\text{Ag}_2$ .

4. Action of developer upon nascent silver bromide from (3)— $30\text{FeC}_2\text{O}_4 + 30\text{AgBr} = 10\text{Fe}_2(\text{C}_2\text{O}_4)_3 + 5\text{Fe}_2\text{Br}_6 + 15\text{Ag}_2$ .

5. Action of nascent silver from (3) upon subjacent silver bromide— $6\text{Ag}_2 + 18\text{AgBr} = 6\text{Ag}_5\text{Br}_3$ .

The reactions expressed in 3, 4 and 5 thus repeat themselves so long as there is any ferrous oxalate to be oxidised. Adopting the method used in the last lecture of indicating the allotropic silver bromide as a wedge, let us suppose that in fig. 65 the intensity of light acting upon different portions of a film of silver bromide was such that in a given time we had at A, e, c, a, B, a layer of altered molecules represented by lines A, ef, cd, ab, BC, in the ratios 0, 1, 2, 3, 4.

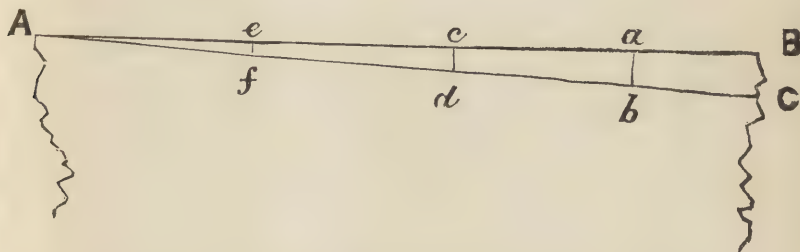


FIG. 65.—GRAPHICAL REPRESENTATION OF DEVELOPMENT BY SLOWLY REDUCED SILVER BROMIDE.

Let us suppose that having exposed the film in such a way that we have twice as many allotropic molecules at B as at c, we then place the film in the developer. Then, at a certain instant of time, we shall have at B and C a deposit of metallic silver and photo-bromide, *approximately* in the ratio of 1:2. But as we continue the development it is evident that the ratios between these lines will completely alter. Suppose, for instance, we keep

on developing until the deposit below B has reached the bottom of the film.

Under these circumstances we shall have at C a deposit of silver and photo-bromide, the thickness of which below c, instead of being half as great as that below B, is now practically the same as it.

If we continue development still further it is evident that the whole of the film will finally consist of metallic silver and photo-bromide, one portion being as dense as another.

Two points which suggest themselves at once from the foregoing considerations are, firstly, that the film itself must be of sufficient thickness and must contain sufficient silver haloid to give the necessary density; and secondly, that there is only one precise instant during development when any two portions of the plate possess certain density ratios.

Supposing, for instance, we wished the density at c in fig 65 to be  $\frac{9}{10}$ ths of that at B, then we should obtain that result only on condition that we stopped the action of the developer at a certain instant of time. If we let the developer act for a shorter time, the density at c would be more than  $\frac{9}{10}$ ths that at B, whilst if we let it act for a longer time the density at c would be less than  $\frac{9}{10}$ ths that at B.

In knowing what the relative densities of different portions of a view are to be, and in knowing when to stop the action of the developer so as to get these densities, the great difficulty of development lies, or to put the matter in the words of an eminent authority "development is an art and a science combined, the art consists in knowing what you want, and the science in knowing how to get it."

A consideration of fig 65, will clearly show the fact that the actual strength of the solution cannot possibly exert any influence upon the final result, save inasmuch as a strong solution will enable a given amount of silver to be reduced in a *shorter time* than if a weak solution had been used.

Let us now consider the effect of adding certain substances to the developer.

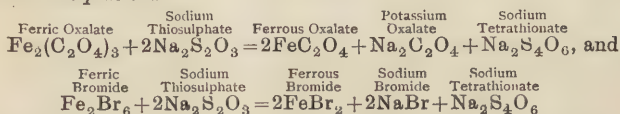
Taking some of this solution of potassio ferrous oxalate I divide it into three portions, and leaving one intact I add to the second a little sodium thiosulphate (hypo), and to the third some potassium bromide.

Next giving this dry plate a short exposure to actinic light I make three marks upon it with each of the solutions, and as you see, the developer containing hypo blackens it at once, the plain developer after some time, and the developer containing bromide not at all, at least, in the time we have permitted it to act. But the whole matter really resolves itself into a question of *time*, for if I leave the plate sufficiently long in contact with the plain oxalate or for very much longer in contact with the oxalate and bromide I shall obtain precisely the same effect as with the oxalate and hypo.



Substances which, like the hypo in this particular instance, accelerate development are spoken of as accelerators, those which like the bromide retard it as restrainers, and it will be necessary to devote some little time to the consideration of the manner in which they act.

We have seen that as a result of the ordinary cycle of operations going on during development, ferric oxalate and ferric bromide are formed. Now both these substances are powerful retarders, and the hypo probably acts by reducing them to ferrous salts in accordance with the equations—



As regards the action of the potassium bromide in retarding development, it probably acts by forming a double salt with the silver bromide, which is acted upon with greater difficulty by silver photo-bromide than pure silver bromide would be. As proof of this I may remind you of the fact that silver bromide is soluble in potassium bromide.

That the image is in the film and not on it admits of direct proof.

I have here a commercial gelatino-bromide dry plate, which has been exposed beneath the black cross, developed, and then soaked in chrome-alum. At the present moment you see the image shows as a white cross on a dense black ground. Immersing the plate in nitric acid I dissolve the metallic silver out of the film whilst the silver bromide remains intact, and on now examining the whole you plainly perceive that the white cross is raised above the remainder of the plate, which has become almost transparent. The white cross consists, in fact, of silver bromide unaffected by the nitric acid, which dissolved away, on the contrary, the metallic silver produced by the action of the developer.

Although I have used silver bromide only in these experiments you must not conclude from this that none of the other haloids are capable of being developed by powerful reducing agents; for, as a matter of fact, both silver iodide and chloride, emulsified in gelatine or collodion, are also capable of being used in conjunction with ferrous oxalate. In fact, just as with the former method of development so with this one, any silver haloids can be developed indifferently by either this method or by the former one. Many other substances are commonly employed instead of potassio-ferrous oxalate. Thus pyrogallol, hydroquinone, or eikonogen rendered alkaline by ammonia, caustic soda or potash, or the carbonates of these metals might be and are commonly employed. The action of these substances is practically the same as that of the potassio-ferrous oxalate, and may be summed up by

saying that they all possess, when rendered alkaline, a strong affinity for oxygen, in virtue of which they can decompose nascent silver bromide into bromine and metallic silver.

#### SYNOPSIS.

*Free silver nitrate stains gelatine.*

*Potassio-ferrous oxalate, alkaline pyro, eikonogen, hydroquinone, etc., develop up an image on an exposed silver haloid in absence of free silver nitrate.*

*This image consists for the most part of metallic silver.*

*The silver constituting the image is derived not from the developer but from the film itself*

*The film of silver haloid must be of a certain thickness and must contain a certain minimum quantity of the haloid used.*

*The action of all so-called alkaline developers is due to their property of absorbing oxygen, or its equivalent of halogen, becoming thereby oxidised at the expense of the halogen of the haloid used.*

*Substances like hypo with ferrous oxalate, or alkalies with pyro, hydroquinone, etc., lessen the time which it takes to complete development. They are consequently called accelerators.*

*Substances like ferric oxalate, potassium bromide, ferric bromide, etc., augment the time necessary to complete development. They are consequently called restrainers.*

*The final result will be the same (although the time taken to bring it about will be different) whether an accelerated, normal, or restrained developer be employed.*

*Any silver haloid can be developed by either acid or alkaline methods.*

*With a given exposure, alkaline development will bring out a picture where acid development would fail to do so.*

## LECTURE XXVI.

VARIATION IN CHARACTER OF NEGATIVE PRODUCED BY UNDER, CORRECT AND OVER EXPOSURE—HURTER AND DRIFFIELD'S RESEARCHES—CONNECTION BETWEEN LIGHT REFLECTED BY ORIGINAL AND DENSITY OF NEGATIVE—CURVES OF TRUE AND FALSE REPRESENTATION—IMPOSSIBILITY OF CORRECTING ERRORS IN EXPOSURE DURING DEVELOPMENT—FACTORS INFLUENCING DURATION OF EXPOSURE—MEASUREMENT OF THE ACTINIC POWER OF LIGHT—THE WATKINS EXPOSURE METER AND THE ACTINOGRAPH.

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IT will be convenient at this stage of our progress to consider the means we must adopt to make negatives giving prints true to nature.

Taking as the simplest possible case three objects reflecting white light only, say a plaster cast draped with dark grey velvet, in front of a light grey background, let us assume that we have placed our camera opposite to it, and are ready to uncap the lens, with the ultimate object of obtaining a print which shall truly represent the whole as the eye sees it.

Now you all know that the duration of the exposure will very materially alter the character of the resulting negative, a too short exposure resulting in what we call a hard negative, *i.e.*, one in which contrasts of light and shade are exaggerated, and an unduly prolonged exposure giving a negative in which these contrasts are not sufficiently emphasised. Evidently the harder the negative the greater the difference, and the flatter the negative the less the difference between the amounts of light reflected from the various portions of the print, and from all this it follows at once that an exposure of a certain definite duration followed by development, stopped at a certain period, will give a negative yielding a print, the different portions of which will reflect light in exactly the same way as the cast, drapery, and background reflected it when the negative was being made.

What relation is there between the amount of light reflected from different portions of the original and the amounts of silver constituting in the negative the image of those portions?

To answer these questions, I have here two black cylinders, which can be made to revolve very rapidly. Upon the circumference of one of these are fastened two pieces of white paper, cut to the shape of right-angled trapezoids, as shown in A fig. 66, and upon the other are fastened two pieces of white paper, cut to the shape of B in the same figure.

Causing the cylinders to revolve, you perceive that the one upon which are pasted the pieces of paper cut like B shows a uniform gradation in tint from pure white to grey, whilst the gradation shown by the other changes somewhat abruptly at the centre.

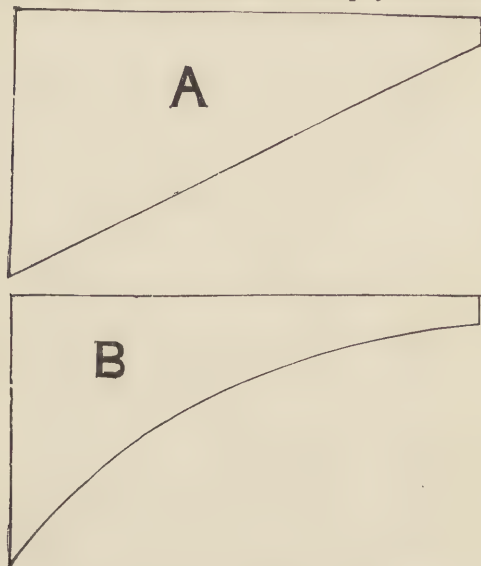


FIG. 66.—HURTER AND DRIFFIELD'S CYLINDERS.

Now an inspection of fig. 66 will reveal the fact that in the cylinder showing uniform gradation the lengths of a series of equidistant vertical lines increase in geometrical progression, *i.e.*, as 1, 2, 4, 8, 16, 32, whilst in the case of the other cylinder these lines increase in arithmetical progression, *i.e.*, as 1, 2, 3, 4, 5, 6, and we learn from the experiment that whenever we see in nature a uniform transition from light to dark we may be sure that the amounts of light reflected from the objects showing this gradation decrease or increase in geometrical and not in arithmetical progression.

Since a negative should be, so far as the amounts of light which different portions of it transmit, the true converse of the original, we see at once that the following relation must hold good between the amounts of light reflected from different portions of the revolving cylinder, showing uniform gradation, and the amounts of



light transmitted by the corresponding portions of a negative made from it. We might in fact put the matter thus:—

Light reflected from revolving cylinder...  $\frac{1}{2} \frac{1}{4} \frac{1}{8} \frac{1}{16} \frac{1}{32}$  ..  $1 \cdot 2 \cdot 4 \cdot 8 \cdot 16 \cdot 32$   
 „ transmitted by correctly-exposed negative of same  $\frac{1}{2} \frac{1}{4} \frac{1}{8} \frac{1}{16} \frac{1}{32}$

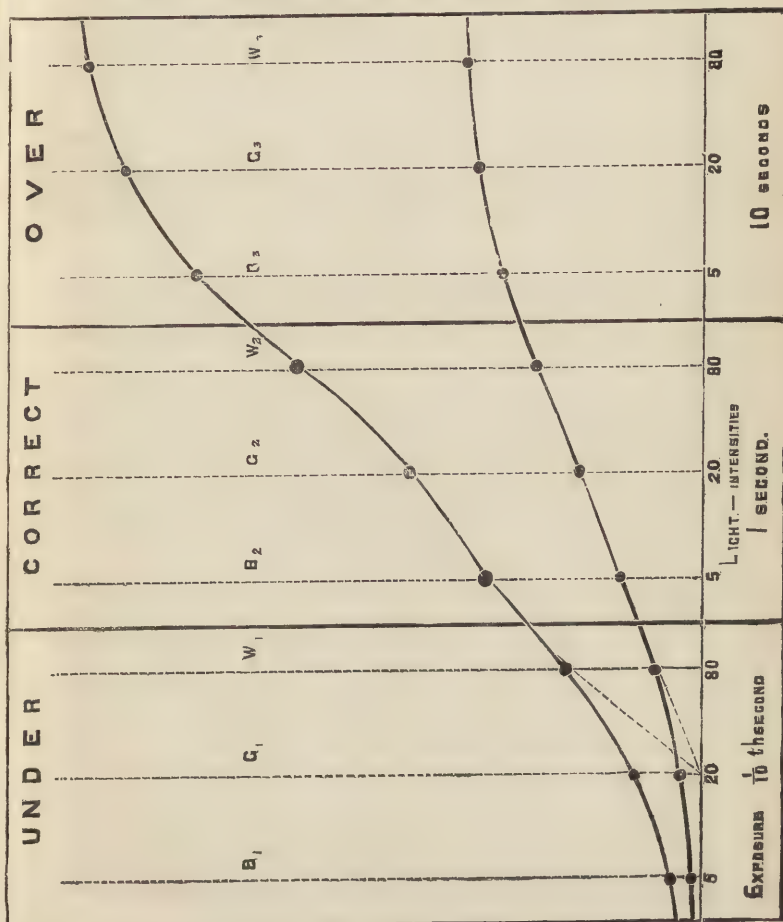


FIG. 67.—HURTER AND DRIFFIELD'S CURVES.

We have still, however, to learn the relation between the amount of light which different portions of a negative transmit and the amount of silver actually present at those portions.

To illustrate the relation holding good in this case, I have here a glass vessel shaped like A in fig. 66, and filled with gelatine jelly, holding in suspension finely divided metallic silver.

If you examine this vessel by transmitted light, you will at once perceive that the light passing through it is in regular gradation from one end to the other, *i.e.*, it transmits light in geometrical progression, although, as we see from its shape, the amount of silver present determining of course the transmitted light, is actually in arithmetical progression.

Calling now the amounts of light reflected by our white cast, drapery, and background, 80, 20, 5, it is evident that a negative will be false in gradation if the density of its different portions are the reciprocals of these figures, or, in fact, in any other ratios than in an arithmetical series corresponding to the given geometrical one.

If we expose for too short a time, then the amount of silver which measures, of course, the density, will be practically proportional to  $80 \cdot 20 \cdot 5$ , as shown in the curve to the left of fig. 67, and such a negative would give a print possessing utterly false gradation.

If, again, we over-expose, the dark drapery becomes almost as dense as the white cast, and we obtain a result shown in the curve to the right hand of figure. But if we correctly expose, *i.e.*, expose in such a way that the light transmitted by the portions of the negative representing the cast, drapery and background are as  $\frac{1}{80}$ ,  $\frac{1}{20}$ ,  $\frac{1}{5}$ , then the amounts of silver will be in the arithmetical progression represented by the central curve in fig. 67.

We put into practical language the results given in these curves by saying that under-exposure gives high lights which are too dense relatively to the shadows.

Can we during development do anything to improve this state of things?

We might and probably would add a large amount of the accelerator (hypo with ferrous oxalate, or alkali with pyro, eikonogen, hydroquinone, &c.), and so fog the portions of the negative, consisting of unchanged silver bromide, upon which the dark drapery should have been impressed, but although we would in this way increase the density of *this* portion relatively to that portion upon which the image of the white cast fell, it is evident that the light grey background would still be false relatively to the white cast and the dark drapery.

Unduly prolonged exposure would give on the other hand insufficient contrast between the densest and least dense portions of the negative. Now to get a normal result we should have beneath that portion of the film upon which the image of the dark drapery fell a smaller number of allotropic molecules than

beneath the portion upon which the image of the white cast fell. By unduly prolonging the exposure, the bromine liberated by the conversion of some of the allotropic molecules at the latter place into silver photo-bromide reconverts in some way some of these allotropic molecules into their normal condition, so that we have now beneath the portions of the film where the image of the white cast fell a smaller number of molecules ready to be attacked by the developer than would have been there had the exposure been normal.

What can we do to remedy this state of things? Evidently we must either increase the number of allotropic molecules beneath the portion of the film upon which the image of the white cast fell, or we must decrease their number beneath the portion of the film upon which the image of the white drapery fell, neither of which methods are, of course, practicable. It might be thought that by adding a restrainer, say potassium bromide, to the developer, we should get what we want.

Let us reason out in what way this would act. We have already learnt that this substance does not *destroy* the developable image, *i.e.*, does not reconvert the allotropic molecules of silver haloid into their original condition, but merely renders it more difficult for the developer to act upon them.

Now, beneath the portions of the film where the image of the dark drapery fell let us assume that we have 100 allotropic molecules, as against 200 where the image of the white cast fell. If we act for a sufficient length of time upon the exposed plate with potassium bromide, prior to applying the developer, we may, it is true, convert the 100 allotropic molecules representing the dark drapery into 100 molecules of the more stable double salt, 100 of the 200 molecules representing the white cast being also converted into the same double salt. On now applying the developer the 100 remaining allotropic molecules representing the white cast will no doubt be the first to be attacked, and we may, by stopping development at this point, obtain a result equivalent to that which would be obtained if the plate had been given an exposure sufficient to allotropise 100 molecules beneath the portions of the film where the image of the white cast fell, but none at all anywhere else. But this result is not, of course, anything likewhich would have been obtained had the exposure been normal.

In other words, the ratios between the number of allotropic molecules at any portion of the film being determined by the time during which light has acted, and by that only, it is out of our power to convert, by variations in the constitution of the developer, the result obtained with over or under exposure into a result the same as that given by correct exposure.

Since, then, to get a perfect negative we must give a correct exposure, a brief consideration of the means to be adopted to get this result will form a fitting sequel to what we have just learnt.

The duration of the exposure requisite to obtain a given result depends upon—

- 1st.—The lens.
- 2nd.—The rapidity of the plate.
- 3rd.—The actinic power of the light.

I have already explained in what way the first factor influences the duration of the exposure, and as regards its second, I may state that the so-called sensitometer numbers, given on the boxes containing commercial plates, afford little or no guide as to the relative rapidities of the plates they contain. Indications are not, however, wanting that before long plate makers will label their plates in a more satisfactory manner.

The last point to be considered is the actinic power of the light. Evidently, the mere *visual* brightness of an object is no guide whatever to its photographic effect, and for this reason the many forms of photometers which have been put upon the market from time to time are worse than useless.

The question then really resolves itself into a measurement of the actinic power of the light, an instrument effecting this being termed an actinometer. Now such an instrument may take two forms. We may make use of the fact that light darkens certain substances, or we may make use of the fact that light causes the temperature of certain coloured substances to rise.

To illustrate an actinometer constructed upon what we may call chemical principles, I have here a slip of paper coated with gelatino-bromide emulsion, and containing also potassium metabisulphite.

Burning some magnesium wire in front of it, you perceive that the paper darkens, the darkening being, in fact, up to a certain point proportional to the actinic power of the light, and to the time during which it has acted.



FIG. 68.—WATKINS' EXPOSURE METER.

Now it is quite easy to match in oil or water colours the exact shade obtained by exposing the paper to light, and as the relation between the actinic power of the light and the darkening of the



paper is more nearly proportional the less the degree of darkening is, an actinometer can be constructed by exposing the bromide emulsion to relatively feeble light, and then painting a piece of paper to match the exact tint obtained.

Such an instrument called the Watkins exposure meter (fig. 68) is on the table, and I prove its correctness in the following manner:—

Placing it twelve inches from my magnesium lamp, I set fire to the magnesium, and keep it burning until the paper darkens to the tint. Previous to the experiment I have marked a couple of yards of the magnesium in inches, and now reading off the number scratched on the end of the magnesium inside the tube, I find it to be 17. Now, placing the instrument so that it is only six inches from the lamp, I repeat the experiment, and again reading the number scratched on the ribbon, I find it to be 21. I have, then, used  $21 - 17 = 4$  inches of magnesium. Now, since I halve the distance the effect should be fourfold as great, *i.e.*, I should have to burn one quarter the amount of magnesium to get the same result, and this is what I have actually found it necessary to do.

We may, however, attack the problem in a different way. A red substance absorbs, broadly speaking, all the rays which act upon a bromide plate, and in so doing becomes heated.

To show this I have here a differential thermometer in one of the bulbs of which is placed ordinary white cotton wool, and in the other cotton wool dyed red.

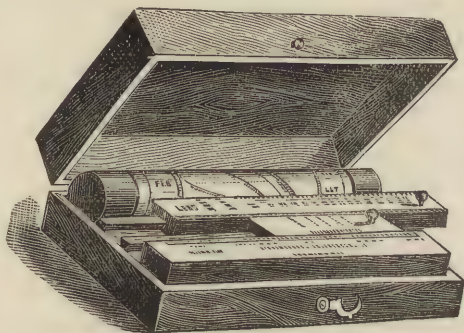


FIG. 69.—THE ACTINOGRAPH.

Both bulbs are at the present moment in water, and are therefore at the same temperature. Lighting my magnesium lamp in front of the beaker containing them, you perceive that we get a distinct rise in temperature in the bulb containing the red wool,

which rise in temperature is a measure of the rays absorbed by the red wool other than the red, and this means, of course, a measure of the actinic effect of the light.\*

This principle has been embodied by Dr. Hurter in the actinometer which bears his name, and by the use of which he has constructed a curve showing the mean values of the light at a certain morning and afternoon hour during the entire year, and this curve he has made use of in his valuable instrument the actinograph, by which correct exposures are reduced to almost mathematic certainty (fig. 69).

#### SUMMARY.

*Under-exposure* results in a negative with *too violent* contrasts, *over-exposure* in one with *insufficient* contrasts, *correct exposure* in one with *contrasts* like the *view itself*.

In every *uniform gradation*, from brightness to shadow, *light* is *reflected* in *geometrical progression*. The *light transmitted* by a *negative* should be the *reciprocal* of that *reflected* from the *view*.

The *amounts of silver* present at different portions of a *negative*, *transmitting light* in *geometrical progression*, are *themselves* in *arithmetical progression*.

Neither *accelerator* nor *restrainer* can alter the *gradations* of any *negative* to what they would be with *correct exposure*—i.e., to obtain the best possible *negative* the *exposure* must be *correct*.

The *duration of exposure* depends upon the *lens*, the *rapidity* of the *plate*, and the *actinic power* of the *light*.

*Photometers* are *useless* for measuring the *actinic power* of the *light*, as they give the *aggregate* of *all* the *rays* constituting *white light*, not the values of only some of them.

An *actinometer* measures the *actinic power* of the *light*—i.e., it gives the value of those *rays only* which *act* upon the *sensitive surface*.

*Bromide emulsion*, mixed with *potassium metabisulphite*, etc., *changes colour* on exposure to *actinic light*, the *rate of change* being up to a certain point *proportional* to the *actinic power* of the *light*, and to the *time* during which the *light* has acted.

The *less* the amount of *actual darkening*, as compared with the *original colour* of the *emulsion*, the *nearer* will the above *ratio* hold *good*.

*Red wool*, *linen*, *glass*, etc., *absorbs* those *rays* which *act* upon the *sensitive plate*, and this *results* in a *rise* in *temperature* practically *proportional* to the *actinic power* of the *light*.

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\* For practically the whole of the subject matter of this lecture I am indebted to the invaluable researches of Dr. Hurter, and his colleague, Mr. Driffield.

## LECTURE XXVII.

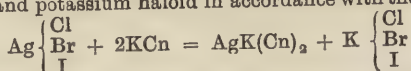
FIXING THE DEVELOPED IMAGE—ACTION OF POTASSIUM CYANIDE AND SODIUM THIOSULPHATE UPON THE SILVER HALOIDS—NECESSITY FOR THE THOROUGH ELIMINATION OF THE FIXING AGENTS—REDUCTION OF THE OVER-DENSE IMAGE BY DISSOLVING AWAY A PORTION OF IT, OR BY REHALOGENISING AND REDEVELOPING IT—COMPARISON OF VARIOUS REDUCTION METHODS.

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TO prevent any alteration of the developed image on subsequent exposure to light, and also to facilitate the production of positives from it, the unaltered silver haloid must be removed from the film.

This operation known as fixing depends upon the fact that certain substances which have little or no action upon metallic silver will convert the insoluble silver haloids into salts soluble in water.

The two fixing agents commonly employed are a five per cent. solution of potassium cyanide, or a 25 % solution of sodium thiosulphate (hypo). To illustrate the action of the potassium cyanide I have here three tubes containing silver chloride, bromide, and iodide respectively, and adding to each some of this solution of cyanide, you perceive that the insoluble haloids disappear, having, in fact, become converted into soluble double cyanides of potassium and silver, and potassium haloid in accordance with the equation—



Potassium cyanide possesses the disadvantage of being exceedingly poisonous, and of attacking the silver of the image more or less, particularly in the half-tones of the negative. To illustrate this latter fact I place some strong solution of potassium cyanide in this test tube covered inside with a very fine layer of metallic silver, when you see that the metal is at once attacked and dissolved.

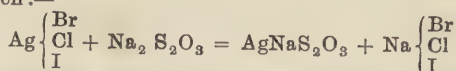
Cyanide can be, and is, commonly used in a solution of the indicated strength for fixing collodion negatives, but cannot very readily be employed with gelatine ones on account of its action upon the gelatine itself. In this latter case sodium thiosulphate is the best substance to employ.

This substance, unlike potassium cyanide, forms two salts with silver, viz., an insoluble and a soluble double thiosulphate.

Adding to this solution of silver nitrate some sodium thiosulphate you perceive that a precipitate falls, which is at first

white, and then passes through various shades of yellow and brown to deep brownish black. The white precipitate is an insoluble double thiosulphate of silver and sodium represented by the formula  $\text{Ag}_2\text{S}_2\text{O}_3 \cdot 2\text{Na}_2\text{S}_2\text{O}_3$ , which very soon, owing to its instability, becomes converted into silver sulphide, sodium sulphate, sulphur dioxide, sulphur and sodium thiosulphate, in accordance with the equation  $\text{Ag}_2\text{S}_2\text{O}_3 \cdot 2\text{Na}_2\text{S}_2\text{O}_3 = \text{Ag}_2\text{S} + \text{Na}_2\text{SO}_4 + \text{SO}_2 + \text{S} + \text{Na}_2\text{S}_2\text{O}_3$ . 2Br<sup>v</sup> 2H

Now adding some silver nitrate to a strong solution of thiosulphate, you perceive that the precipitate first formed immediately dissolves in the liquid, and the same final result is obtained when I add the thiosulphate to these three tubes containing silver chloride, bromide, and iodide respectively. The change occurring in both cases consists in the conversion of the silver into soluble silver sodium thiosulphate, and the action of sodium thiosulphate upon the silver haloids can be represented by the following equation:—



When using sodium thiosulphate as a fixing agent, we must therefore employ a fairly concentrated solution to avoid any risk of the formation of insoluble silver sodium thiosulphate.

The fixing agents will also act upon the trace of silver photo-bromide remaining in the film, converting it into metallic silver and soluble double cyanide or thiosulphate, according to the equations just given.

Before fixing, we have, then, in the film silver haloid, silver photo-haloid, and silver; after fixing, metallic silver only.

Whichever fixing agent is employed, every trace of it must finally be removed by washing the negative in running water, an operation usually effected in an apparatus in which the water is kept in constant motion.

If this precaution be neglected, the residue of the cyanide or hypo remaining in the film will gradually attack the silver, and besides these substances would, by their presence, seriously interfere with the subsequent operations of printing. With hypo we must also permit the negative to remain in the solution until every trace of unchanged silver haloid has been dissolved out, otherwise there is a risk of the silver haloid remaining in the film reacting upon the hypo with the probable formation of the insoluble double salt.

With the object of avoiding the somewhat tedious washing necessary to remove every trace of hypo from a gelatine film, it has been proposed to apply to the film a solution of certain substances which decompose hypo. One of the best of these is hydrogen peroxide, which reacts upon and oxidises the hypo without exerting any influence upon the silver itself. Other substances, such as bromine or chlorine water, or the alkaline hypochlorites, will certainly decompose hypo, but as they rehalogenise the film as



well, it is easy to see that their employment cannot be recommended.

Negatives developed with pyro and fixed in hypo stain this latter more or less, to avoid which many operators mix the hypo with some sodium bisulphite, say one part of bisulphite to four parts of hypo, and the addition has much to recommend it, as pyro developed negatives fixed in such a solution are cleared as well as fixed, and the fixing bath itself remains colourless to the last.

Ammonium and potassium sulphocyanate and sodium sulphite have been also employed for fixing purposes, but possess little or no advantage over the older fixing agents.

It frequently happens that, owing to development having been continued for too long a time, the gradations of the negative are not what is required.

In a case of this sort recourse must be had to some method of reducing the density of the deposit. Methods of effecting this may be conveniently sub-divided into four groups:—

- 1st. Methods of directly dissolving the deposit.
- 2nd. Methods of indirectly dissolving the deposit.
- 3rd. Methods of rehalogenising the deposit and then dissolving it.
- 4th. Methods of rehalogenising the deposit and then redeveloping it.

As regards the first method, we may leave the plate for a sufficient length of time in the fixing bath of cyanide or hypo, when the metallic silver will gradually dissolve and the negative will consequently become reduced in density. To illustrate this method, I place this collodion negative in the strong solution of potassium cyanide contained in the glass trough in the lantern, when, as you see, it becomes gradually thinner and thinner, and would end by being altogether obliterated.

Instead of cyanide I might have employed hypo, when the same effect would take place, only more slowly.

It has been found in practice that if a negative immersed in a fixing bath be removed from time to time so as to permit the atmosphere to act upon the film, it will become much more rapidly reduced than if maintained constantly immersed beneath the surface of the solution.

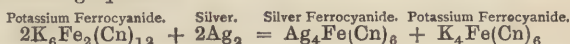
Instead of a fixing bath, a rather dilute solution of nitric acid might be employed, and would answer fairly well with a collodion negative, but not with a gelatino-bromide one, on account of the action of the acid upon the gelatine.

A more rapid plan of reducing density consists in mixing the fixing bath with something which will convert the silver haloid into a compound capable of being rapidly dissolved by the cyanide or hypo.

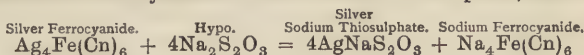
Placing a crystal of iodine in this solution of potassium cyanide, obtain, as you see, a colourless liquid which contains, in fact, potassium iodide (KI) and cyanogen iodide (CNI), mixed with an excess of potassium cyanide. Diluting this liquid somewhat, I

pour it into the glass trough in the lantern containing a collodion negative, when you see that the density rapidly decreases, and finally the image completely disappears. The action here is a relatively simple one, the cyanogen iodide converting the silver of the image into a mixture of silver cyanide and iodide, which substances the potassium cyanide at once attacks. I may mention, in passing, that a concentrated solution of cyanogen iodide is the best substance for removing silver stains from the hands, but care must be taken that no cuts are present on the portions of the skin on which it is being employed.

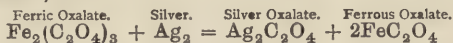
Placing a crystal of potassium ferricyanide in this solution of hypo, you see that no visible interaction between the two substances has occurred, and pouring the mixture over the small gelatino-bromide negative in the trough in the lantern, you see that a gradual reduction in density takes place. In this case the potassium ferricyanide becomes converted into ferrocyanide, with the simultaneous conversion of the silver into silver ferrocyanide, a change expressed by the following equation:—



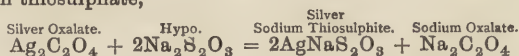
and then the hypo attacks the silver ferrocyanide, converting it into sodium ferrocyanide and silver sodium thiosulphate, thus—



Another method consists in mixing ferric oxalate with hypo, whereby the silver becomes converted into silver oxalate and ferrous oxalate, thus—



the silver oxalate being at once converted by the hypo into silver sodium thiosulphate,



As an example of the third method, viz., rehalogenising the deposit, and then subsequently dissolving away a portion of it, I place this small fixed and washed negative in the glass trough in the lantern, and cover it with a solution of cupric chloride, strongly acidulated with hydrochloric acid, when you see that the image gradually becomes fainter and fainter, owing to the chlorination of the metallic silver. The action is represented by the following equation:— $2\text{Ag} + 2\text{CuCl}_2 = \text{Cu}_2\text{Cl}_2 + 2\text{Ag}$ , the cuprous chloride dissolving in the excess of hydrochloric acid. Now, washing off the solution, I pour over the plate some potassium cyanide, when you see that the silver chloride gradually dissolves.

I might have employed cupric bromide, ferric chloride or bromide, calcium hypochlorite, or chlorine or bromine water,

instead of the cupric chloride, all of which substances would rehalogenise the metallic silver, and instead of cyanide I might have used hypo. The difficulty in this method of reducing density is to know when to stop the rehalogenisation of the silver, for the final result not being apparent until the cyanide or hypo are applied, it often happens that the negative is reduced too much, and utterly ruined.

A far better plan consists in rehalogenising the deposit, washing it, and then redeveloping, taking care to avoid too great density.

A convenient solution for effecting this contains one ounce of potassium bichromate and three ounces of strong hydrochloric acid, mixed with one hundred ounces of water. Pouring this mixture over the small gelatine negative in the lantern trough, you see that the deposit is soon bleached throughout. Now, washing off the bleaching solution, I pour over the negative a rather dilute solution of ferrous oxalate, when you see that the silver chloride gradually blackens, and would eventually develop up to exactly the same density as at first. We can, however, stop development at any moment we please, so as to get any requisite reduction in density. It is evident that if this method is adopted the negative must be finally again fixed to remove the unaltered silver haloid.

It is interesting to notice in this connection that it is by no means necessary to re-expose the halogenised silver to actinic light in order to render it capable of being redeveloped.

To illustrate this point I cause the red light to be turned on, and I then place this finished negative in the mixture of hydrochloric acid and bichromate until completely bleached. Now, washing it free from the bichromate, I plunge the plate into ferrous oxalate, when you see that the deposit develops up to full intensity, although it has not been exposed to actinic light at all.

It is evident that any method of reduction involving the dissolving out of some of the material of the image must change the relative densities at different portions of the negative; hence a negative which has been over-developed, although it can be improved by reducing its density, can never be brought back to exactly the condition in which it would have been if the development had been originally stopped at the right instant.

If, however, the entire film is rehalogenised and development is then recommenced, it is possible to obtain a negative identical with the one which would be obtained if development had not originally been carried too far, and this fact renders the fourth method the only satisfactory one to adopt in practice.

#### SUMMARY.

*Potassium cyanide* converts the *insoluble silver haloids* into *soluble double cyanides*.

*Sodium thiosulphate* (hypo) in excess converts them into *soluble double thiosulphates*.

*Dilute hypo* converts the *silver haloids* into *insoluble salts*, and

the same thing occurs if an *excess* of the *haloids* is mixed with a little *hypo*.

The *fixing agent* must be *completely* got rid of, otherwise the *silver* will be gradually dissolved.

The *safest* plan to get rid of the *fixing agent* is to *well wash* the film in plain *water*.

*Pyro* developed negatives *stain* the *hypo* bath. To avoid this, the *hypo* may be mixed with *sodium bisulphite*.

*Over-dense* negatives may be reduced by dissolving out some of the *metallic silver*.

*Over-dense* negatives may also be reduced by *halogenising* the entire deposit, and then redeveloping it to proper density. The latter method is the only one *scientifically correct* in principle.

The *halogenation* of the deposit is conveniently effected by a mixture of *hydrochloric acid* and *potassium bichromate*, which converts *silver* into *silver chloride*.



## LECTURE XXVIII.

INTENSIFICATION—CLASSIFICATION OF METHODS OF CARRYING THIS OUT—DEPOSITION OF SILVER ON ORIGINAL DEPOSIT EITHER FROM ACID OR ALKALINE SOLUTION—BLEACHING OF DEPOSIT BY MERCURIC CHLORIDE, &c., AND SUBSEQUENT BLACKENING OF THE BLEACHED DEPOSIT—CHAPMAN JONES'S RESEARCHES ON INTENSIFICATION—METHODS DEPENDING ON THE CONVERSION OF THE METALLIC DEPOSIT INTO SUBSTANCES POSSESSING A MORE HIGHLY ACTINIC COLOUR—COMPARISON OF METHODS.

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IN the last lecture we considered the means available for reducing a negative which, owing to development having been carried too far, was over-dense, and we must now learn how the converse problem can be solved, viz., how a negative too weak, owing to development not having been pushed far enough, may be strengthened, or intensified, as we photographically put it.

We may conveniently classify intensification methods as follows:

1. Methods in which metallic silver is deposited from above upon the silver image.

2. Methods in which the silver image is converted into silver chloride and some other insoluble substance which must, however, as well as the silver chloride, admit of being subsequently darkened by a suitable reagent.

3. Methods in which the silver chloride is converted into, or coated with, some other substance possessing greater actinic opacity.

As exemplifying the first method, I place in the cell in the lantern a small fixed and washed collodion negative, and pour over it a solution containing two grains of citric acid, and the same quantity of pyrogallol in an ounce of water, mixed with two or three drops of a 5 per cent. solution of silver nitrate, when, as you see, the negative gradually gains in intensity, and can, if left long enough in the solution, be made as dense as we please.

The explanation of the change which is taking place is exceedingly simple. The pyro and silver nitrate react upon each other, and constitute the two elements of a voltaic couple which precipitate metallic silver upon the silver of the image. The action is, in fact, identical with that which takes place during wet plate development.

Any other metal slowly depositing from its solution in this way would serve instead of the silver, to prove which I place another collodion negative in a fresh cell, and pour over it the same mixture of pyro and citric acid, adding, however, a little mercurous

nitrate, instead of silver nitrate, when, as you see, a practically identical result is obtained, mercury being deposited instead of silver.

This method of intensification, although very good for a collodion plate, is not quite so practicable when applied to a silver haloid in gelatine, the reason being that this latter substance is liable to become stained by the silver nitrate. If, however, the gelatine film is first of all hardened by being immersed for some time in a solution of white alum. strongly acidified with hydrochloric acid, and to which a few drops of a solution of iodine in potassium iodide have been added, to decompose any traces of hypo remaining in the film, then the process answers perfectly.

To prove this, I project on the screen a glass cell containing a thin gelatine negative, which has been treated in the way just described, and is, at present, being intensified in a similar mixture to that which served for the collodion plate.

Since, however, in spite of all care some traces of silver nitrate will combine with the gelatine, it is indispensable to refix all gelatine negatives intensified in this way so as to leave nothing in the film capable of being subsequently acted upon by light.

Evidently, since it is the free silver nitrate which stains the gelatine, we should be able to avoid this mishap by applying a solution containing silver in some other state of combination.

Thus, for instance, if silver bromide is dissolved almost to saturation in hypo, the solution of silver sodium thiosulphate will, when applied to a plate, gradually intensify it, the action being here quite similar to the action of the pyro and silver nitrate, with the important difference that no staining can occur.

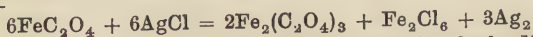
You will remember that in the last lecture it was pointed out that cupric and ferric chlorides will chlorinise metallic silver, becoming themselves converted into cuprous and ferrous compounds. These latter chlorides being under the given conditions soluble in the liquid used no intensification results upon subsequent development; but if we employ mercuric chloride for chlorinising the image the conditions are altered somewhat.

Adding hydrochloric acid to a solution of mercurous nitrate, we obtain, as you see, a white precipitate, which remains undissolved even on adding a large excess of hydrochloric acid. This substance is mercurous chloride or calomel, and pouring over some of it contained in the second tube a little of the usual potassio-ferrous oxalate developer, you see that it is blackened, a change due to its decomposition into metallic mercury and chlorine, the latter serving to oxidise the ferrous oxalate thus—



A change quite similar takes place when ferrous oxalate reacts upon silver chloride. The equation has been already

given, but for convenience of reference we will repeat here—



Now, pouring some mercuric chloride over the finely divided metallic silver contained in this tube, you see that it is bleached. There is good reason for believing that this change is represented by the following equation:  $\text{Ag} + \text{HgCl}_2 = \text{AgHgCl}_2$ , the bleached substance being a true double chloride of silver and mercury.\*

Decanting off the liquid from the white substance at the bottom, I pour some potassio-ferrous oxalate over it, when you see that it at once blackens the double chloride, behaving towards it, in fact, just as it would to each chloride separately, *i.e.*, it converts them into metallic silver and metallic mercury. You will readily understand from this what happens when a negative is placed in mercuric chloride slightly acidulated with hydrochloric acid, and when thoroughly bleached then treated with potassio-ferrous oxalate.

To carry out the whole process before you, I immerse this gelatino-bromide negative in mercuric chloride, when, as you see, it gradually bleaches. The deposit at this stage consists of the silver-mercurous chloride. Washing off the mercuric chloride, I now apply the ferrous oxalate, when, as you see, a gradual blackening occurs, at the completion of which we have upon the negative the same amount of silver as at first, plus a certain amount of mercury derived from the mercurous chloride.

Clearly, therefore, we have gained density equivalent to this amount of mercury, and, since the silver is still there, we can, if we wish, go through the process again and again, until the density is judged to be sufficient.

Other methods of blackening the silver-mercurous chloride might be adopted. To illustrate this, I have here a bromide print which has been bleached by mercuric chloride. Dividing it into four portions I immerse them in (1) sodium sulphite, (2) ammonia, (3) potassio-silver cyanide, (4) ammonium sulphide, and you see that in each case the bleached image has blackened.

The action of sodium sulphite upon silver-mercurous chloride is capable of being expressed by the following equation:— $4\text{HgAgCl}_2 = 3\text{HgCl}_2 + 2\text{AgCl} + \text{Ag}_2\text{Hg}$ , the mercurous chloride and silver chloride so formed being dissolved out by the sodium sulphite, and the silver and mercury constituting the intensified image. It will be observed that half the silver of the image is exchanged for mercury, four atoms of silver giving two of silver and one of mercury, a result which generally, but not always, results in intensification. This process repeated over and over again, will result in the gradual exchange of the silver of the image for more and more mercury, the action soon ceasing, however, owing to the relatively small amount of silver present. Unlike

\* Chapman Jones, in *British Journal of Photography*, 1890, page 88.

† Chapman Jones, *loc. cit.*

potassio-ferrous oxalate, sodium sulphite will not, therefore, give increasing densities each time it is applied.

To illustrate the action of the ammonia I add some of this substance to calomel contained in this tube, when you see that it becomes blackened, the change being due to its conversion into black dimercurous-ammonium chloride, in accordance with the equation:—

Mercuric Chloride.	Ammonia.	Ammonium Chloride.	Dimercurous Ammonium Chloride.
$\text{Hg}_2\text{Cl}_2$	$+ 2\text{NH}_3$	$= \text{NH}_4\text{Cl}$	$+ \text{NH}_2\text{Hg}_2\text{Cl}$

the silver chloride remaining practically unchanged. It is evident, therefore, that this method does not admit of repetition.

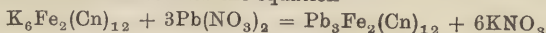
The action of the potassio-silver cyanide is probably as follows\*:—  
 $\text{Hg}_2\text{Cl}_2 + 2\text{AgK}(\text{Cn})_2 = \text{Ag}_2 + 2\text{Hg}(\text{Cn})_2 + 2\text{KCN}.$

Since, in this case, the mercury of the mercurous chloride enters into solution with the precipitation of an equivalent quantity of silver, it is clear that we have the original amount of silver, plus an amount equal to it, and this being the case the process should admit of being repeated any number of times, which appears to be actually the case.

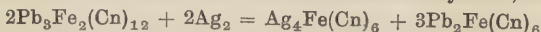
The ammonium sulphide acts by converting the mercurous silver chloride into the corresponding sulphide thus,  $\text{HgAgCl}_2 + (\text{NH}_4)_2\text{S} = 2\text{NH}_4\text{Cl} + \text{HgAgS}$ , the mixed sulphides forming the intensified deposit.

Another method of intensification capable of giving great density at one operation consists in converting the silver deposit into lead and silver ferrocyanides, and then blackening both of these by ammonium sulphide.

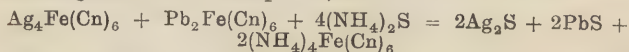
Mixing this solution of lead nitrate with one of potassium ferricyanide, I obtain in solution lead ferricyanide and potassium nitrate in accordance with the equation—



and placing a gelatine negative in the mixture, you perceive that the colour of the deposit gradually changes to yellowish white, owing to the conversion of the metallic silver into silver ferrocyanide, with the simultaneous formation of insoluble lead ferrocyanide, thus—



To illustrate the next part of the process I have here a negative which has been bleached in this way, and then very thoroughly washed, and immersing it in ammonium sulphide you see it becomes very greatly intensified, the silver and lead ferrocyanides becoming converted into sulphides, thus—



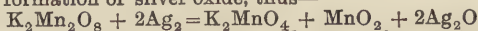
The last method of intensification we have to consider depends, you will remember, upon the possibility of coating the silver image

\* Meldola's "Chemistry of Photography," page 356.



with some substance of greater actinic opacity than itself, or of converting it wholly into such a substance.

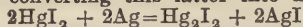
To illustrate this method I place this collodion negative in a 1% solution of potassium permanganate, when you see that the colour gradually changes from grey to brownish yellow, the action being due to the fact that the metallic silver reduces the permanganate to manganese peroxide, with probably the simultaneous formation of silver oxide, thus—



the silver oxide and manganese peroxide possessing greater opacity than the metallic silver alone.

This method, although suitable for collodion, does not answer with gelatine, owing to the staining of the latter by the permanganate.

Another method belonging to the same class, and capable of being used with gelatine negatives, consists in using a solution of mercuric iodide in potassium iodide. To illustrate this I place this small gelatine negative in such a solution, when you see that the deposit gradually becomes brown. The action here appears to be due to the silver combining with one of the iodine atoms of the mercuric iodide, converting this latter into mercurous iodide, thus—



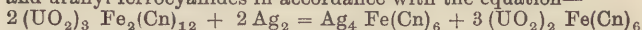
the silver iodide probably forming a double salt with the mercurous iodide, and so rendering it more stable than it is in the pure state.

Instead of employing a solution of mercuric iodide in potassium iodide, a solution of mercuric iodide in hypo may be used instead, and gives practically the same result, but is more convenient, as the negative to be intensified may be at once placed in the mixture without the trouble of washing it to free it from hypo—a precaution absolutely necessary when using any other method which depends upon the action of mercuric chloride, etc., upon metallic silver.

To illustrate the reason of this I add a solution of mercuric chloride to one of sodium thiosulphate, when you see that a white precipitate falls. If, then, mercuric chloride were poured over a negative not perfectly free from hypo, this white precipitate would be formed throughout the film, and as this substance changes colour on the application of most of the usual blackening agents (sodium sulphite, ammonia, etc.), the result would be a very bad case of staining. For a similar reason, in methods belonging to the second class and involving the use of mercuric chloride, followed by something else, it is essential to get rid of every trace of mercuric chloride before the blackening agent is applied.

Another method of intensification applicable to collodion or gelatine negatives consists in converting the silver deposit into silver ferrocyanide and uranyl ferrocyanide. Mixing a solution of uranyl nitrate with one of potassium ferricyanide, I obtain uranyl ferricyanide in solution, thus— $\text{K}_6\text{Fe}_2(\text{Cn})_{12} + 3\text{UO}_2(\text{NO}_3)_2 = (\text{UO}_2)_3\text{Fe}_2(\text{Cn})_{12} + 6\text{KNO}_3$ . Now pouring the liquid over an ordinary gelatine negative the silver deposit gradually changes to

brownish red owing to its gradual conversion into insoluble silver and uranyl ferrocyanides in accordance with the equation—



Uranyl ferrocyanide being of a highly non-actinic colour, no subsequent blackening is necessary, as was the case when a lead salt was used.

A moment's consideration of the principles laid down in the last lecture will render it evident that the only one of all these methods of intensification which will not alter the *relative* densities of the different portions of the negative is the method depending upon the bleaching of the image by mercuric chloride, and its subsequent darkening by the application of potassio-ferrous oxalate.

If, then, a negative has been correctly exposed but under-developed this is the method to employ. If, on the other hand, the exposure has been exceeded, use should be made of the lead or uranium intensifiers, diluted as occasion may demand. A negative intensified with uranium must not be washed for too long a time after intensification, as the uranium ferrocyanide is not wholly insoluble in water.

#### SUMMARY.

*Slowly depositing metallic silver will intensify any negative. Silver nitrate is liable to stain gelatine, hence special precautions must be employed to prevent this during intensification.*

*Silver bromide in hypo does not stain gelatine.*

*Mercurous chloride is blackened by ammonia, potassio-ferrous oxalate, &c.*

*Metallic silver converts soluble mercuric chloride into insoluble mercurous chloride, the silver becoming silver chloride.*

*Potassio-ferrous oxalate converts mercurous silver chloride into silver and mercury.*

*Bleaching by mercuric chloride, followed by blackening by potassio-ferrous oxalate, can be repeated as often as may be desired.*

*Mercuric chloride is itself attacked by potassio-ferrous oxalate, and must in consequence be thoroughly washed out of the film after the bleaching action is complete.*

*The bleaching of the film by the mercuric chloride must be thorough, otherwise the relative densities of different portions of the negative will be altered.*

*Lead ferricyanide converts silver into insoluble silver ferrocyanide with the simultaneous production of insoluble lead ferrocyanide.*

*Lead and silver ferrocyanides are blackened by ammonium sulphide.*

*Potassium permanganate is partially deoxidised by metallic silver.*

*Mercuric iodide is partially deiodised by metallic silver.*

*Uranyl ferricyanide converts silver into insoluble silver ferrocyanide with the simultaneous production of insoluble uranyl ferrocyanide.*

*Uranyl ferrocyanide is of a highly non-actinic red-brown colour.*

*Uranyl ferrocyanide is not completely insoluble in water.*

## LECTURE XXIX

THE PRODUCTION OF POSITIVES—METHODS BY DEVELOPMENT—PRINTING-OUT METHODS—PRINTS AND TRANSPARENCIES—ENLARGEMENTS—COLLODION LANTERN SLIDES—PLAIN DEVELOPED PRINTS ON PAPER—THE PHOTO-CRAYON PROCESS—COLLODIO-CHLORIDE AND GELATINO-BROMIDE EMULSION PROCESSES.

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A NEGATIVE is, as you will remember, only a means to an end, that end being the production of a positive which shall truthfully represent the original.

A positive may be suitable for viewing by transmitted or reflected light. As an example of the first kind of positive, I project on the screen a collodion transparency, and the prints made by different processes which you see on the table are examples of the second.

To make a positive we may proceed in one of two ways, according as that positive is to be of the same size as, or larger or smaller than, the negative we use. In the first case it is merely necessary to place the negative in a printing frame in contact with a sensitive material of some description spread upon paper, glass, &c., and expose the whole to actinic light.

Then, if the material is sufficiently sensitive, we may, with a relatively short exposure, obtain an impression which, although invisible, can be made visible by development, or with a relatively insensitive material we may prolong the exposure, and obtain a visible or printed-out image, as we call it.

The first method is only available with salts of silver; the second, with salts of silver and with certain compounds of iron, gelatine, potassium dichromate, &c.

If our object is to obtain a positive larger or smaller than the original we may evenly illuminate the negative from behind, and cause its enlarged or diminished image to be projected by means of a lens upon a suitable sensitive surface, and so obtain an image capable of being developed, or if the light is very intense, we may even obtain a printed-out image in this way.

In the present lecture we shall only consider the production of developed positives, reserving the production of printed-out images for future consideration.

To illustrate the method employed to obtain a positive the same size as the original, I place in contact with this negative a sheet of Ilford bromide paper, which is merely paper coated with an emulsion of certain silver haloids in gelatine, and exposing the whole for a few seconds in front of this gas flame, I then place the exposed paper in the potassio-ferrous oxalate developer, when, as you see, I obtain a positive developed print.

To illustrate how a positive smaller than the original is produced I place this view negative in front of the condenser of my lantern, in which position, you remember, it is evenly illuminated. On the small easel facing the lantern is a sheet of cardboard, two inches square, and upon this I focus the image as sharply as possible. Now capping the lantern lens I substitute for the cardboard a Thomas transparency plate, and giving an exposure of about three seconds, I recap the lens and place the plate in the potassio-ferrous oxalate, when I obtain, as you see, a positive image smaller than the original. This method is, in fact, the one commonly adopted to make lantern transparencies from negatives of any size, and instead of employing a condenser between the source of light and the negative, this latter might be caused to face the clear sky in ordinary daylight, or placed in front of a sheet of white paper, inclined at an angle of  $45^\circ$ , the small image being received on the ground glass of the camera in the usual way. Clearly in the case in point the size of the image depends purely upon the relative distances of the negative and sensitive surface from the lens.

Placing upon my easel a sheet of cardboard,  $18 \times 24$  inches, I substitute for the view negative a small portrait head and shoulders, and moving off the easel, and at the same time bringing the projecting lens nearer to the negative, I cause the enlarged image to just fill the requisite space. Now capping the lens I substitute for the cardboard a sheet of Ilford paper, and giving an exposure of about two minutes, I develop, when you see that an enlarged positive is the result.

Operating by daylight I might have illuminated the negative just as if I was making a transparency, receiving the enlarged image on the ground glass of a large camera, or I might place the negative in the window of my dark room, which we will suppose faces the sky, and cause it to project an image on an easel placed in the dark room.

Of the great value of these enlargements there can be no question, for, being given a small and perfectly sharp negative, we can, by suitably stopping down the lens with which we enlarge, render the circle of definition in the enlargement exactly the same as that of the eye looking at the original view, and then, provided the gradations of negative and enlargement are correct, and agree with those of the view itself, we should obtain the truest representation which it is probably in the power of photography to give.

Evidently we might make from the original negative another equally sharp positive, and, using this to project an enlarged image upon a second sensitive plate, we should obtain an enlarged negative from which prints could be made by any process.

It will be convenient to begin by studying the conditions to be fulfilled in making transparencies or prints on silver haloids developed by the so-called acid method.

It is evident to begin with that, since the highest lights of the



subject, if pure white, must be represented by complete absence of deposit, the exposure must be so regulated as to yield this result, and since, moreover, the blackest shadows of any view always show some detail, the degree of concentration of the developer and the duration of development must be so adjusted as to yield sufficient, but by no means excessive, density.

Taking first of all the production of a transparency, the collodion contains the following ingredients:—

Ether alcohol	..	..	..	..	1 ounce.
Ammonium iodide	..	..	..	..	4 grains.
Cadmium bromide	..	..	..	..	2 grains.
Pyroxyline	..	..	..	..	4 grains.

and a perfectly clean glass plate coated with this collodion is sensitised in a 20-grain bath, washed free from nitrate, coated with the coffee preservative as already described, and then dried. After exposure the preservative is washed off, and the plate developed in the following developer:—

Pyro..	..	..	..	..	1 grain.
Citric acid	..	..	..	..	2 "
Water	..	..	..	..	1 ounce.
Silver nitrate	..	2 drops of a 10-grain solution.			

the exposure being so regulated that development is complete in about fifteen minutes.

The object of the bromide in the collodion is here to prevent excessive density, and the object of prolonged development with a minimum of silver nitrate is to give fineness of deposit, for upon this much of the artistic beauty of a transparency depends. After development, the plate is washed and fixed in either hypo or, preferably, dilute cyanide.

I have here some plates prepared in this way, and placing one of them in contact with this negative, I expose the whole to the light of the burning magnesium, then develop and fix the plate, and project the transparency upon the screen.

To make prints by a method of this sort, the following solution\* is made use of, in which sheets of suitable paper are steeped for several hours, and then dried:—

Sodium chloride	..	..	..	..	6 grains.
Potassium iodide	..	..	..	..	2 "
Ammonium bromide	..	..	..	..	1 grain.
Water	..	..	..	..	10 ounces.

When thoroughly dry the paper is floated for three minutes on a solution of silver nitrate made up as follows:—

Silver nitrate	..	..	..	..	60 grains.
Citric acid	..	..	..	..	1 grain.
Water	..	..	..	..	1 ounce.

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\*Abney. "Instruction in Photograph," page 257.

And finally developed after exposure with a pyro-developer, the same as that just used.

Unfortunately, the great tendency of the paper to become stained during development is a drawback to the employment of this process, but we may easily obtain excellent positives by reflected light in another way.

Taking this glass plate I coat it with collodion made up as follows:—

Ether-alcohol	..	..	..	..	1 oz.
Pyroxilin	..	..	..	..	4 grs.
Cadmium iodide	..	..	..	..	2 "
Ammonium iodide	..	..	..	..	1 "
Cadmium bromide	..	..	..	..	$\frac{2}{3}$ "
Ammonium bromide	..	..	..	..	$\frac{1}{3}$ "

and sensitise it in a 20-grain bath. Now, draining it as completely as possible, I place a piece of blotting paper at each of the corners, and then put this portrait negative with a vignetting mask over the whole. Next, burning a little magnesium wire over the negative, I then place the wet plate in the following developer:—

Pyrogallol	..	..	..	..	5 grains.
Citric acid	..	..	..	..	3 "
Glacial acetic acid	..	..	..	..	50 minims.
Water	..	..	..	..	1 ounce.

and when developed I fix the image in a strong solution of hypo. Washing off the greater part of the hypo under the tap, I rapidly dry the film by holding it over the Bunsen burner, and, placing in contact with it this sheet of cream-coloured blotting paper, you perceive that the image looks as if it was on the surface of the paper, and not on the glass, the result being a positive by reflected light seen through a glass plate.

This method of working constitutes the photo-crayon process, and with care gives results which are probably unsurpassed by any other process.

Turning now to emulsion processes, an emulsion of silver chloride in collodion gives excellent results for either prints or transparencies.

To illustrate this method of working\* I have here a solution containing—

Ether-alcohol	..	..	..	..	1 oz.
Magnesium chloride	..	..	..	..	30 grs.
Pyroxilin	..	..	..	..	6 "
Aqua regia	..	..	..	..	5 minims.

And into this I emulsify in small quantities at a time, the following solution—

Silver nitrate	..	..	..	..	30 grs.
Boiling water	..	..	..	..	60 minims.
Ether-alcohol	..	..	..	..	1 oz.
Pyroxilin	..	..	..	..	6 grs.

\* Eder und Pizzighelli. "Die Photographie mit Chlorsilber und Chemischer Entwickelung."

Properly speaking I should permit the emulsion to ripen for a day, but omitting that precaution I pour the whole into 20 ounces of water contained in this large beaker when, as you see, the pyroxilin is precipitated carrying with it the silver chloride. It merely remains to collect the pellicle, which will keep for any length of time, and dissolve it as required in the proportion of one grain for every 20 minims of ether-alcohol. The emulsion is then spread over glass or paper, and next coated with a preservative made by mixing albumen (white of egg) with five times its volume of water, and then dried, being developed after exposure with ferrous ammonium citrate, ferrous potassium citrate, ferrous citro-oxalate or hydroquinone.

To illustrate this I show you a transparency and a print prepared by this process.

We next come to gelatino-bromide emulsion processes. As examples of plates and paper coated with these, we have Thomas's transparency plates and the Ilford positive papers, both of which contain a mixture of silver haloids, in which the bromide predominates and can be developed with potassio-ferrous oxalate, ikonogen, hydroquinone, or generally speaking, with any developer which is suitable for the development of negatives on the same emulsion.

The chief point to attend to in the preparation of such an emulsion is to make a product giving absolutely pure high lights. This is done by using an excess of soluble iodide and of gelatine, as in the following formula:—\*

A.				
Potassium iodide	..	..	..	46 grains.
Potassium bromide	..	..	..	698 "
Gelatine	..	..	..	3410 "
Water	..	..	..	18 ounces.

B.				
Silver nitrate	..	..	..	1162½ grains.
Water	..	..	..	9 ounces.

As a developer for transparencies, ferrous oxalate is probably unsurpassed, and for prints or enlargements the same developer, rather diluted, or a weak solution of ikonogen, answers well.

It is found in practice that to get first-class results by this method, the exposure must be very accurately timed.

If the exposure is too short the colour is good, but the shadow details are missing, and the relative densities are exaggerated; whilst on the other hand if the exposure is too long, the shadow tails are there but the colour is bad, the high lights are degraded, and the relative densities are again altered, the shadows not being black enough.

To illustrate these points I have on the table six bromide prints which have been given exposures gradually increasing in arithmetical progression. Comparing colour only, you perceive that the

\* Liesegang. "Die Bromsilber-gelatine."

prints which have received the shortest exposure are the best, the colour becoming more and more brown as the exposure is increased; whilst comparing gradation you see that the prints which are of a good black colour are precisely those in which the gradation is utterly false. Generally speaking, a bromide print or enlargement which truly renders the gradations of a negative is not black but brown, and it requires the utmost skill of the operator to so adjust his developer to his exposure, or *vice versa*, as to get a result in which the gradations are correct and this colour at the same time good.

#### SUMMARY.

A negative is only a means to an end, this being the production of a positive.

A transparency is a positive viewed by transmitted light, a print a positive on paper viewed by reflected light.

Transparencies or prints are made by similar processes.

Silver nitrate has a tendency to stain paper, hence prints developed by acid development are rarely good.

A transparency on glass, backed with paper, gives the same impression as a print on the paper itself.

Cyanide tends to give the silver deposit a white colour, and is therefore unsuitable for fixing positives by reflected light.

A good print should reflect light, as the original reflected it.

A transparency in which the opacities are the true reciprocals of the opacities of the negative from which it is made should, if the same size as that negative, show no picture at all when both are placed film to film.

In bromide printing short exposure gives good colour but bad gradation, a longer exposure good gradation but bad colour.

Enlargements can be made from small, perfectly sharp negatives in which the circle of definition coincides with that of the eye when viewing the original.



## LECTURE XXX.

METHODS OF PRODUCING POSITIVES BY PRINTING-OUT—DIFFERENCE BETWEEN THE DARKENED PRODUCT PRODUCED BY DEVELOPMENT AND BY PRINTING-OUT—NECESSITY FOR PAPER FREE FROM HYPO AND METALLIC PARTICLES—RIVES AND SAXE'S PHOTOGRAPHIC PAPERS—PRINTING-OUT ON SO-CALLED PLAIN AND ALBUMINISED PAPER—"PRESERVED" SENSITISED PAPER—COLLODIO AND GELATINO CHLORIDE PRINTING-OUT EMULSIONS.

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IN the last lecture we considered the method to be followed in preparing sensitive surfaces containing silver haloids, and yielding developed positives. We must now learn how to prepare surfaces yielding printed-out images by comparatively prolonged exposures. The fundamental difference between the two methods lies in the fact that in the first case no energetic halogen absorbents are present, the invisible image consisting of allotropic silver haloids, yielding on development deposits consisting for the most part of metallic silver.

In printed-out methods, on the other hand, an excess of an energetic halogen absorbent, usually silver nitrate, is present, and the visible image doubtless consists of a mixture of metallic silver and silver photo haloid or photo salt, the latter predominating in quantity. Again, whilst in developed methods all the silver haloids are available, in printing-out methods the chloride only is found to be of much use, the bromide and iodide giving printed-out image too feeble to be of any value.

Taking, to begin with, the production of positives by reflected light or prints, the first consideration is a specially-prepared paper quite free from hypo and from metallic particles. Hypo is employed frequently as an antichlor. to get rid of the excess of chlorine employed in bleaching the rag pulp prior to its conversion into paper, and if present gives rise to much trouble, whilst metallic particles derived from the rollers employed in calendering the paper will act as nuclei for the deposition of silver, producing innumerable stains.

Since it is the free silver nitrate which is acted upon by the hypo and metallic particles, it follows that far more care must be employed in the selection of paper for use in printing-out processes than would be necessary if the paper was going to be employed merely as a support for emulsion containing no free silver nitrate.

Fortunately excellent paper is met with in commerce, and is called "Rives," if made at the French town of that name by

Blanchet Brothers, or "Saxe," when made at Malmédy in Rhenish Prussia by Steinbach & Co. To illustrate the absolute necessity for good paper I have on the table two pieces of paper, one of which is pure white and the other stained brown and all covered with spots. These were originally pieces of Rives paper and of ordinary note paper, which two days since were steeped in a strong solution of silver nitrate and then dried, when you see that the hypo, etc., present in the inferior paper has reduced more or less of the silver nitrate.

As supplied commercially neither Rives nor Saxe paper is sized, the sizing being effected by the photographer himself. This consists of arrowroot, albumen, pyroxilin, etc. Gelatine is decidedly objectionable owing to its action upon silver nitrate.

I will begin by showing you how what is called a plain paper print is made.

In this vessel I have dissolved, in half-an-ounce of water, 80 grains of barium chloride and 1 grain of citric acid, and I pour this mixture over 60 grains of Bermuda arrowroot contained in this beaker, and mix the whole intimately with a glass rod.

In the beaker over the Bunsen burner there is, on the other hand,  $4\frac{1}{2}$  ounces of water, and causing this to boil, I add to it the arrowroot paste, and boil the whole until a clear liquid results.

The whole is then permitted to get quite cold, when it partly solidifies to the viscous liquid which you see in the other beaker, and which was prepared in an exactly similar way.

To use this I remove the tough pellicle at the top, and having pinned the Rives paper to a clean drawing-board, I spread the mixture over it with a sponge. In this state the paper is said to be salted, and will keep indefinitely.

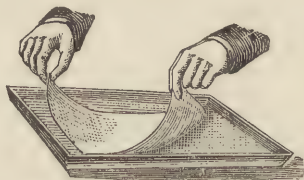
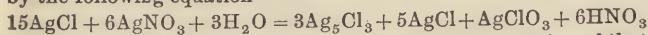


FIG. 70.—SENSITISING THE PAPER.

To sensitise I float it for four minutes (fig. 70) on a 60-grain solution of silver nitrate, and when dry the paper is ready for exposure under a negative, the result being a print similar to the one which you see on the table.

The barium chloride here reacts upon the silver nitrate thus— $\text{BaCl}_2 + 2 \text{AgNO}_3 = 2 \text{AgCl} + \text{Ba} (\text{NO}_3)_2$ , the excess of silver nitrate with which the paper remains impregnated acting as the

chlorine absorbent, the change during exposure being represented by the following equation—



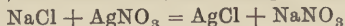
the products being silver chloride, derived from the portion of that material on the paper itself, and some derived from the silver nitrate, together with silver chlorate, nitric acid, a residue of silver nitrate and the dark image of silver photo bromide.

Instead of using arrowroot as sizing, I might have employed albumen, and should then have ordinary albuminised paper as it is called.

To illustrate this method of working, I have here a liquid containing 44 grains of common salt, dissolved in 4 ounces of white of egg, mixed with 1 ounce of water, the whole having been first beaten up to a froth, then permitted to settle, and finally very carefully filtered.

Placing some of this solution in a dish, I float a sheet of Rives paper upon it for five minutes, then remove it carefully and hang it up to dry, when I obtain so-called albuminised paper, which will keep for any length of time.

To sensitise this, it is floated as before on a sixty-grain solution of silver nitrate, and then dried, the change being represented by



The silver nitrate here again plays the part of a chlorine absorbent, and upon exposing the paper to light beneath a negative, we get a printed-out image such as the one you see on the table, the change produced being similar to that which occurred in the former case.

The arrowroot and albumen play no doubt an important part in this process, for besides their effect in sizing the paper, there is good reason for believing that certain compounds they contain combine with the silver of the silver nitrate, and so largely modify the colour of the finished print.

The insoluble precipitate obtained when silver nitrate is mixed with albumen becomes reddish-brown on exposure to light, whilst it is found that although arrowroot is not precipitated by silver nitrate, nevertheless the colour of a print made upon paper sized with arrowroot is distinctly bluer than the colour of one made upon unsized paper. All these results point to the fact that the change in question is not quite so simple as I have assumed it to be, but as to what the precise change is, we are as yet in the dark.

The solution of silver nitrate employed in sensitising the paper becomes altered by use. In the first place, some of the albumen, etc., dissolves in the solution, and imparts to it a dark colour, but this can be completely removed by shaking up the bath with a little silver carbonate. Evidently each sheet of paper sensitised takes up mechanically some of the solution, and at the same time converts a certain quantity of the silver nitrate into an equivalent quantity of barium or sodium nitrate.

Although at first sight it might seem that a final result similar to that which obtained with wet collodion baths would hold good here, in practice this is not so, for if the quantity of silver nitrate present is less than about 7 per cent., the albumen is dissolved by the silver nitrate—a result particularly undesirable. On this account it is essential to strengthen the bath from time to time by adding silver nitrate to it, 40 grains of this substance being usually added for every piece of paper, 18 × 24 inches, sensitised on the solution. Paper sensitised by either of these methods does not keep, but must be used within a day or two of preparation. If it is a question of preserving the paper, this may be done by floating the back of it on a 7 per cent. solution of citric acid or, better still, on a 4 per cent. solution of sodium citrate.

Tartaric acid, either alone or mixed with citric acid, has also been recommended.

These substances evidently act by converting the free silver nitrate into silver citrate or tartrate, which, as we will learn in a moment, can act as their own sensitisers, or as sensitisers for silver chloride.

Evidently pyroxylin could be used to keep the silver chloride upon the surface of the paper, and presents the advantage over arrowroot or albumen that the chloride could be emulsified and the paper, etc., coated with the emulsion at one operation.

Curiously enough, the nature of the soluble chloride employed in making the emulsion is found to affect the colour of the positive. Thus, magnesium chloride gives a greyish calcium chloride a brown, cadmium chloride a violet, strontium chloride a sepia, lithium chloride a sepia red deposit, and this fact in itself shows how much more remains to be done before the action of light upon the silver haloids can be said to be thoroughly understood.

The nitrates of all these metals being deliquescent, staining of the negative is very liable to occur during printing, for which reason it is preferable to employ the hydrochlorate of cinchonine in the collodion.

To illustrate the preparation of an emulsion of this nature I dissolve in this tube 120 grains of silver nitrate in two drachms of water, and add the solution to 120 grains of pyroxilin dissolved in ten ounces of alcohol-ether. Next dissolving 60 grains of cinchonine hydrochlorate and 15 grains of tartaric acid in the half-ounce of alcohol contained in this other tube, I emulsify the cinchonine into the collodion, and then adding a drachm of glycerine I obtain an emulsion ready for being spread upon paper or glass, using, however, a much thicker coating than would be necessary if the emulsion was to be developed.

The excess of silver nitrate, aided probably by the tartaric acid, here plays the part of sensitiser. It might be thought that the excess of silver nitrate crystallising out of the film would be inconvenient, but in practice it is found that the small quantity of glycerine obviates any trouble on that account.



Instead of making the emulsion in the manner just indicated, an emulsion might be made with any metallic chloride and ammonium citrate, then washed in the ordinary way, and redissolved, the plates being coated with a preservative of sodium sulphite or potassium nitrite, but this plan presents no advantage over the one just described.

It is found in practice that considerable difficulty is experienced in coating paper direct with collodio-chloride emulsion owing to the repellant action of the alcohol-ether upon the paper, but all trouble is avoided if the paper is given a preliminary coating of 575 grains of precipitated barium sulphate emulsified into 1,150 grains of soft gelatine dissolved in 50 ounces of water. The barium sulphate here renders the image more vigorous, both by the contrast of the deposit over a white surface and by preventing the silver nitrate from being absorbed by the paper.

There would evidently be a decided gain, both in economy and in ease of coating the paper by employing the emulsion of silver-chloride in gelatine, and this is found quite practicable.

To prepare such an emulsion the following formula may be made use of\*—

1.				
Sodium chloride	..	..	..	40 grains.
Potassium citrate	..	..	..	20 "
Water .. ..	..	..	..	1 ounce.
2.				
Silver nitrate	..	..	..	120 grains.
Water .. ..	..	..	..	1 ounce.
3.				
Nelson's No. 1 gelatine	..	..	..	320 grains.
Water .. ..	..	..	..	3½ ounces.

The silver nitrate having been mixed with the gelatine, previously swelled and melted, the sodium chloride and potassium citrate are emulsified into the mixture, and the whole then boiled for ten minutes and washed, etc., just as if a negative emulsion was being made.

You will observe that in this formula the chloride and citrate are in excess, consequently, there is no free silver nitrate to attack the gelatine, and, owing to the fact that paper or glass coated with this emulsion yields a vigorous image, it is evident that the true sensitiser is here the silver citrate.

Instead of employing sodium chloride, ammonium chloride might have been used, and potassium oxalate could be substituted for the citrate.

Instead of coating paper or glass with such an emulsion, calico or linen might be employed, provided it had been previously coated with a ten per cent solution of gelatine, containing a little chrome alum, followed by a second coating, containing some barium

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\* Abney, "Instruction in Photography," p. 288.

sulphate. For coating paper, however, no special precautions are necessary. To get sufficiently vigorous results, all these emulsions must be spread over the support in relatively thick layers, the necessity for which is of course almost self-evident.

#### SUMMARY.

The deposit constituting the visible printed-out image on silver chloride is silver photo-chloride.

Paper for sensitising in presence of free silver nitrate must be free from *hypos*, and from metallic particles; papers for receiving emulsion, containing no free silver nitrate, need not be so pure.

Rives and Saxe paper is unsized, the sizing being applied during the salting. The sizing may consist of arrowroot, or of albumen, gelatine is unsuitable in presence of free silver nitrate.

The object of sizing is to keep the image on the surface of the paper.

Albuminised paper is paper coated with albumen or white of egg, and a soluble chloride.

Albuminised paper is sensitised by floating it on a solution of silver nitrate.

Paper containing free silver nitrate does not keep.

Preserved sensitised paper can be made by converting the free silver nitrate into silver citrate or tartrate.

The particular sizing employed, *i.e.*, arrowroot, albumen, etc., influences the colour of the image.

Solutions of silver nitrate containing less than 7 per cent. of the salt dissolve albumen.

Collodio-chloride emulsion for printing-out contains silver chloride and free silver nitrate, etc., or the latter may be washed out, and potassium nitrite, etc., used as preservative.

The particular soluble chloride employed influences the colour of the image.

The nitrates of metals whose chlorides dissolve in ether alcohol are deliquescent.

Cinchonine nitrate is not deliquescent, and cinchonine hydrochlorate is soluble in ether alcohol.

Collodio-chloride emulsion does not spread readily over paper.

Gelatino-chloride emulsion for printing-out contains silver chloride and citrate or chloride and oxalate, but no free silver nitrate.

Gelatino-chloride emulsion is readily spread over paper.

## LECTURE XXXI.

TONING—DIFFERENCE IN COMPOSITION OF DEVELOPED AND PRINTED-OUT IMAGE—TONING BROMIDE PRINTS WITH PLATINUM OR GOLD—NECESSITY FOR ABSENCE OF FERROUS OXALATE AND OF HYPO—CONVERSION OF A SILVER IMAGE INTO RED PHOTO-CHLORIDE—TONING THIS WITH GOLD OR PLATINUM—NECESSITY IN MOST CASES FOR SO-CALLED ALKALINE GOLD TONING BATHS—REASONS FOR THIS—TONING WITH AUROUS AND PLATINOUS SALTS.

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THE final colour of a print or transparency is very frequently far from pleasant. Thus, bromide prints exposed so as to yield correct gradation are generally too brown, whilst prints on albuminised paper, if fixed only, are of a disagreeable foxy red.

Again, from an artistic point of view, it may be thought desirable to modify the colour of any particular result, and in toning we possess a means of doing so without, at the same time, materially affecting gradation.

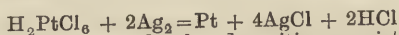
We must begin this subject with a clear understanding that an essential difference exists between a developed and a printed-out positive, the deposit on the first consisting mainly of metallic silver, that on the latter mainly of silver photo-chloride, for which reason a method of toning suited to one would be quite unsuited to the other.

To illustrate the fundamental principle underlying one method of toning deposits of metallic silver, I place in each of these two tubes some finely-divided metallic silver, and then pour into one of the tubes a little chloro-platinic acid rendered slightly acid with nitric acid.

Decanting off the liquid after a minute or so, I wash the residue by decantation, and then pour over it some nitric acid, adding at the same time some of the acid to the other tube. In the one case, as you see, red fumes are evolved, and the powder, metallic silver, dissolves, whilst in the other no action at all takes place.

What is the explanation of this result?

Simply that the platinum of the chloro-platinic acid has exchanged places with the metallic silver in accordance with the equation.



Now the deposit upon a developed positive consists of metallic silver, no matter what the actual colour of that deposit may be, and it follows, therefore, that since metallic platinum precipitated

in this way is always black, it should be possible to alter the objectionable brown colour of any developed positive by simply placing it in a solution of chloro-platinic acid.

To show you that this is actually the case, I place half of this brownish bromide print in such a solution, when, as you see, on removing it, the brown deposit has been changed to a dead black.

To succeed with this or any similar method of toning, the print must be free from every trace of hypo. To show you that the presence of hypo prevents toning, I add to this solution of chloro-platinic acid a few drops of that substance, and then place another brownish print in the mixture, when you will see that no toning will take place in any reasonable time.

The cause of this is not difficult to understand. Toning takes place because the metallic silver on the print deoxidises the chloro-platinic acid, but if hypo is present, this latter, being also a deoxidising agent, acts upon the chloro-platinic acid, first deoxidising it, and then probably converting it into a thiosulphate of platinum.

Since, therefore, the positive must be absolutely free from hypo, if toning is to take place, it becomes essential to wash it very thoroughly before placing it in the toning solution, but this tedious washing may be completely avoided by placing the positive in the toning solution after development and before fixation.

You remember, of course, that the developed deposit consists, before fixing, of silver haloid, silver photo-haloid and silver. The silver haloid itself is, in this case, inert, whilst the silver photo-haloid and the metallic silver, this latter constituting by far the greater portion of the deposit, become toned in the way just pointed out. Mixing now some potassio-ferrous oxalate with the solution of chloro-platinic acid, and then warming the mixture, you perceive that a black precipitate forms. The developer deoxidises, in fact, the platinum solution, and it therefore follows that stains might, and do, occur if any developer remains in the pores of the paper when the latter is placed in the platinum solution.

To avoid this mishap in carrying out the process in practice, the print is placed in one per cent. nitric acid after rinsing off the developer, transferred from that to the toning solution, left there for 15 minutes, again washed, and finally fixed in the usual way.\*

The same process can be applied to transparencies whose colour is unsatisfactory, and gives equally certain results, and since silver bromide is practically unacted upon by light in presence of nitric acid, the toning can be carried on in ordinary diffused daylight. Instead of using platinum various other metals may be employed, and largely modify the final colour. Thus, an acidified solution of gold trichloride acts in a similar way, but gives a blue positive, which simulates a moonlight effect very well. In this latter case, since gold combines with gelatine, it is absolutely

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\* Leaper "Photography Annual" for 1891, page 201.

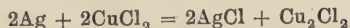


necessary if gelatine is the support to tone before fixing, otherwise the gelatine becomes badly stained.

If the fixed and washed print is immersed in a rather dilute solution of uranyl ferricyanide, made in a similar way to that employed in intensification (*vide* page 217), a brownish-red tone will be obtained.

Another method of obtaining a great variety of tones consists in bleaching out the image by immersing it in a solution of cupric chloride,  $\text{CuCl}_2$ , and then redeveloping it with ferrous oxalate, or converting the bleached deposit into silver photo-chloride, and toning this by the so-called alkaline methods employed with albuminised paper.

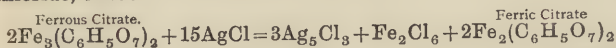
To illustrate this method of working I place this brownish bromide print in a solution of cupric chloride acidulated with hydrochloric acid, when, as you see, the image gradually disappears, the silver being here chlorised at the expense of a portion of the chlorine of the cupric chloride, thus—



the cuprous chloride dissolving in the excess of hydrochloric acid.

Now, rinsing the print in water, I apply to it the usual ferrous oxalate developer, when the print develops up a dead black.

If, instead of redeveloping the bleached print, it had been exposed to light beneath a solution of ferrous citrate, this latter would become oxidised to ferric citrate and ferric chloride; the bleached deposit becomes gradually converted into red silver photo-chloride, thus :—



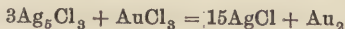
On fixing, we should have a print of a rather pleasant reddish colour, or, instead of fixing the print, we might have first toned and then fixed it, and so obtained a result very like that got with ordinary albuminised paper.\*

Placing this red bromide print, the silver deposit upon which has been converted into silver photo-chloride in the manner just indicated, in an acidified solution of gold chloride, you perceive that the image becomes reduced very considerably in intensity, and changes meanwhile in colour to an unpleasant slaty blue. An acid toning bath is, in fact, quite unsuitable in this case, for reasons which will be apparent in a moment.

Now, placing another print in a solution of gold trichloride, rendered alkaline with sodium carbonate, you perceive that the toning proceeds regularly, with very little reduction in density and we might, by stopping the toning at certain stages, obtain a print of any colour, from a sepia red to a purple black, as you will see from the specimens on the table.

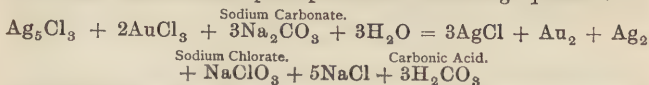
\* Leaper, "Anthony's International Bulletin" for 1891, page 192.

Why must we use an alkaline bath in this case? With an acid bath toning certainly occurs, but is accompanied by a very considerable loss in density, and it is found impossible to produce anything but slaty blue tones. In this case, in fact, the silver photo-chloride reduces the gold trichloride in accordance with the following equation:—



The deposition of metallic gold being accompanied by the simultaneous decomposition of the dark coloured photo-chloride into colourless silver chloride. Hence a great reduction in density is inevitable.

But by mixing the gold trichloride with something capable of being acted upon by chlorine, say sodium carbonate, then a very different change occurs. The sodium carbonate in this case, and not the silver photo-chloride, reacts upon the chlorine of the gold trichloride in accordance perhaps with the following equation:—

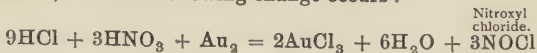


It is evident that in this case less reduction in density would occur, since the deposition of every atom of gold is accompanied by the separation of an atom of silver from the silver photo-chloride.

Instead of employing sodium carbonate as the chlorine absorbent, I might have used sodium phosphate, benzoate, tungstate, acetate or bborate (borax), calcium hypochlorite, ammonium or potassium sulphocyanate, and probably many other substances.

It is found practically that each agent exerts a particular effect upon the final colour, but the explanation of this curious result is not known.

Gold trichloride is itself made by dissolving gold in a mixture of four volumes strong hydrochloric acid, and one volume strong nitric acid, when the following change occurs:—

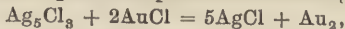


It is essential that the excess of acid be completely driven off by evaporating to dryness, then adding more water and again evaporating to dryness.

By mixing a solution of gold trichloride with an excess of precipitated chalk, and leaving the whole in contact for several days, the yellowish liquid becomes almost colourless, and the solution now contains gold proto-chloride formed thus—



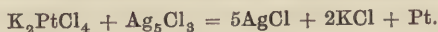
The liquid so obtained serves for toning in plain aqueous solutions, its action upon silver photo-chloride being represented by



from which equation it will be seen that two atoms of gold are

precipitated for every molecule of silver photo-chloride decomposed, instead of for every three molecules, as would be the case when gold trichloride is used. In consequence of this, little reduction in intensity occurs, and the solution gives a beautiful violet black tone to the silver photo-chloride by merely diluting it with water and applying it to the surface.

Instead of a solution of gold protochloride one of platinous chloride or its salt, potassium chloroplatinite, may be used, and gives a dead black colour, the change being represented by—



To illustrate this method of toning I place another of the red prints in this dilute solution of potassium chloroplatinite, acidified with phosphoric acid, when, as you see, it gradually changes to a deep black.

Platinic chloride, on the other hand, just like gold trichloride, is unsuitable for toning silver photo-chloride; although, as you remember, platinic and auric salts answer perfectly when it is a question of toning metallic silver, and not its photo-chloride. Platinous salts are, however, rather expensive, so that from a practical point of view it is more economical to convert a platinic into the corresponding platinous salt, and then use the solution for toning.

Such a change is readily brought about by sodium hypophosphite, and to illustrate it I have in this vessel 30 grains of platinic chloride dissolved in eight ounces of water, and adding to the liquid 20 grains of sodium hypophosphite I boil the whole until the golden colour of the liquid changes to grey. The liquid now contains platinous chloride, and it is only necessary to acidify it with phosphoric acid in order to render it available for toning silver photo-chloride. Care must be taken to use a quantity of hypophosphite not greater than  $\frac{1}{3}$ ds the weight of platinic chloride taken, otherwise some metallic platinum will be precipitated.

#### SUMMARY.

*A developed image consists of metallic silver, a printed out one of silver photo salt.*

*Silver throws down platinum from its solutions.*

*Toning consists in altering the colour of the developed or printed out image.*

*Hypo, or any so-called alkaline developer, reduces solutions of platinum or of gold.*

*Platinum or gold in acid solutions tone silver deposits dead-black or blue.*

*Toning with gold on an organic basis must be performed before fixing, toning with platinum before or after fixing.*

*A silver image of any colour bleached by chlorine always redevelops up black.*

*Silver chloride* exposed to light in contact with *ferrous citrate* becomes converted into *red silver photo-chloride*.

*Gold trichloride* in *alkaline solution* tones *silver photo-chloride* of any colour from *red* to *purple*.

*Gold trichloride* in *acid solution* also tones *silver photo-chloride*, but at the same time greatly reduces the density of the deposit.

A gold toning bath contains *gold trichloride* with *sodium carbonate*, *borax*, *potassium sulphocyanate*, &c., &c.

*Gold proto-chloride* (*aurous chloride*) in *acid solution* tones *silver photo-chloride* with comparatively little reduction in density.

*Chloroplatinic acid* reduces the density of the *photo-chloride* image very much, *chloroplatinous acid* very little.

*Sodium hypophosphite* converts *chloroplatinic* into *chloroplatinous acid*.



## LECTURE XXXII.

USUAL METHODS OF OBTAINING SILVER PHOTO-CHLORIDE—TONING PRINTS ON COLLODIO-CHLORIDE—NECESSITY FOR OVER-PRINTING—INTERFERENCE OF FREE SILVER NITRATE WITH TONING—TONING PLAIN PAPER PRINTS WITH PLATINUM—TONING PRINTS ON ALBUMINISED PAPER—NECESSITY FOR ELIMINATION OF ACID BEFORE FIXING—NECESSITY FOR A THOROUGH CONVERSION OF SILVER CHLORIDE AND PHOTO-CHLORIDE INTO SOLUBLE SALTS DURING FIXING—CAUSES OF THE FADING OF PRINTS—TESTS FOR SILVER SALTS IN A PRINT AND FOR ACIDS AND HYPO IN MOUNTS.

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IN the last lecture we considered the fundamental principles underlying the operation of toning as applied to metallic silver, or to silver photo-chloride. In practice, however, we do not obtain the latter substance in the indirect way indicated in that lecture. In everyday work we obtain that substance mixed with certain other organic salts of silver whenever we expose silver chloride to light in presence of silver nitrate, or of some other halogen absorbent.

Let us take as the first example of a print in silver photo salt this print on collodio-chloride emulsion, prepared as previously indicated.

You will observe, to begin with, that the print seems very much denser than we should finally like it to be. This seeming over-printing is, however, an absolute necessity, for, as we learnt in the last lecture, a considerable loss in density occurs in toning, and, as we shall learn in a moment, a further loss of density occurs on fixing.

We may then take it as axiomatic that every printed out positive must be denser on coming from the printing frame than it is intended finally to be, and this adjustment of the initial density to suit every case is probably one of the most difficult problems which the beginner in photography is called upon to solve.

Now the film itself contains silver nitrate, and this substance would react upon the chlorides of gold or platinum, with the double effect of precipitating the metals they contain, and of throwing down insoluble silver chloride upon the surface of the print. It is, therefore, absolutely necessary to eliminate all the free silver nitrate by washing the print before toning is commenced.

Placing the print in ordinary tap water to remove the free silver

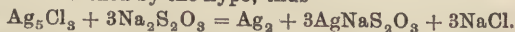
nitrate you see that the water turns milky. Such water contains, in fact, certain soluble chlorides which inter-act with the free silver nitrate, forming insoluble silver chloride.

I have here a second print similar to the first, but which has been thoroughly washed, and I now place this print in the following toning bath :—

Ammonium sulphocyanate	..	..	150	grs.
Gold trichloride	..	..	3	„
Water..	..	..	16	ozs.

And in this you see that the image becomes first yellow, and almost disappears, and then gains in density, and gradually changes through various shades of brown to a fine purple black.

The print being now toned, I place it in a ten per cent. solution of hypo, and in this you see a further reduction in density occurs. You are already familiar with the precise manner in which the hypo acts; it merely remains, therefore, to point out that the loss in density is due to the fact that the residue of silver photo-chloride is attacked by the hypo, thus—



Instead of hypo, sodium sulphite or magnesium chloride might be employed, but in much more concentrated solutions.

Taking now, as an example of platinum toning, this print on arrowroot-sized paper, you will observe that it is printed more deeply than the one just toned, the reason being that, as has been explained in the previous chapter, a greater loss in density occurs during platinum toning in acid solutions than during gold toning in alkaline ones.

Here is another print made in the same way, but thoroughly freed by washing from every trace of silver nitrate, and this I now place in the following toning bath :—

Potassium chloroplatinite	..	..	30	grains.
Glacial phosphoric acid	..	..	80	„
Water	..	..	40	ounces.

And, in this, you see that it gradually changes colour, becoming eventually a dead black, the density being meanwhile very considerably reduced. Fixing the print in hypo after a slight washing in water to get rid of the phosphoric acid, you perceive that very little reduction in density now occurs, the reason being that practically the whole of the silver photo-chloride has been converted into silver chloride and metallic platinum.

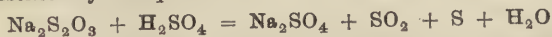
Taking now three well-washed prints on albuminised paper, I place one in the chloroplatinite bath just given, the other in a solution of gold trichloride rendered acid with hydrochloric acid, and the third in the following alkaline toning bath :—

Sodium carbonate	..	..	60	grains
Gold trichloride ..	..	..	3	„
Water	..	..	30	ounces.

The results obtained in the three cases are, as you see, very different and highly instructive. In the platinum bath the print has toned to a dead black, but the density is considerably reduced; in the acid gold bath the print has toned to a slaty blue, but has become nearly obliterated owing to the great loss in density, whilst in the alkaline toning bath the colour is now a purple-black, and only a comparatively slight reduction has taken place.

Mixing some sulphuric acid with a solution of hypo you see that a precipitate occurs, a pungent smelling gas being meanwhile liberated.

Sodium thiosulphate is, in fact, decomposed by this and by most other acids with the liberation of sulphur dioxide and the precipitation of sulphur, the change in this particular case being represented by the equation—



Now sulphur dioxide and sulphur, particularly in the so-called nascent state, react upon metallic silver, forming silver sulphite and sulphide, the latter a black compound, the former a colourless one, the sulphite being, however, the compound which would be most readily formed.

You will understand, therefore, that if a print containing an acid was placed in the hypo a very considerable reduction in density would occur, and, moreover, the silver chloride present in the whites of the print would become converted into silver sulphite, a substance readily yellowed by light.

To show you that such is the case I remove this unfixed print from the dilute sulphuric acid in which it had been placed and immerse it in hypo, when, as you see, it becomes very considerably bleached.

It is essential, therefore, when the platinum or any other acid toning bath is used, to very carefully wash the prints before immersing them in the hypo, otherwise a reduction in density and a yellowing of the whites is certain to occur.

Since every print toned removes from the toning bath a certain quantity of platinum or of gold, it becomes necessary to add some fresh platinum or gold chlorides from time to time. The actual quantity of precious metal taken up will evidently depend upon the extent to which toning has taken place, but, as a general rule, it may be stated that every sheet of paper, 18 × 24 inches, removes from the toning solutions from  $\frac{1}{3}$  grain to 1 grain of gold or platinum.

Platinum is always deposited black, but the exact colour of the deposited gold depends upon the quantity of gold present and the rate at which it is deposited, this latter being greatly influenced by both the depth to which printing has been carried and by the temperature of the toning bath.

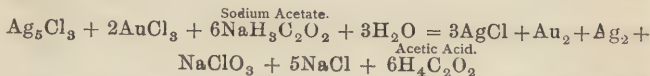
Speaking generally, the colour of deposited gold varies with the size of its particles. If these are very small, their colour is

reddish; if large, blue; consequently, a rather faint print will never tone to a dark colour, and any print toned in a solution containing too little gold or at too low a temperature will always incline to red.

Silver albuminate, in fact, becomes red upon exposure to light, as the print on the table shows, and the whole object of toning with gold is to change the objectionable red colour of the photo-albuminate to a more pleasant hue.

Evidently to do this we require a negative of a certain density and a toning bath of a minimum degree of concentration, and at such a temperature that toning will proceed at a fairly rapid rate. The necessary degree of concentration has been arrived at by direct experiment, the result being the formulæ just given, and as regards temperature, it may be said that a toning bath at a lower temperature than 20°C will not do its work properly.

Again, the rate at which the gold is deposited will also depend upon the degree of acidity of the bath. The more acid this is the more slowly will toning take place, acids acting, in fact, as restrainers. For this latter reason it is essential in using toning baths made up with borax, sodium phosphate, or acetate, or other substances, which, by their interaction with the gold trichloride and silver photo-chloride, liberate an acid, to neutralise this acid from time to time by the addition of a sufficient quantity of sodium carbonate. Taking, for instance, as a type of such a bath, a solution containing sodium acetate and gold trichloride, the following change would occur:—



Since, in such a case, acetic acid accumulates in the toning solution, after a time toning becomes exceedingly slow, to avoid which the bath must be neutralised with sodium carbonate.

A similar change would occur with any salt but sodium carbonate, for the carbonic acid, liberated in a toning bath containing this substance would be soon decomposed at ordinary temperatures into carbon dioxide and water.

Each piece of paper fixed in the hypo converts some of this substance into silver sodium thiosulphate and sodium chloride, and it is evident therefore that fixing baths, as they get old become gradually weaker and weaker. Speaking generally, every sheet of paper 18 × 24 inches requires at least an ounce and a half of hypo to fix it, and it follows from this that hypo baths continuously used for fixing albuminised paper must be strengthened by adding that quantity of hypo for every sheet of paper 18 × 24 inches or its equivalent fixed in such baths.

As already pointed out, every trace of hypo must be completely eliminated from the fixed prints if permanency is aimed at, the reason for this being both that hypo slowly attacks metallic silver,



and that silver sodium thiosulphate is gradually altered in contact with light and air. An imperfectly washed print containing these substances would tend, therefore, to become eventually obliterated; and, in addition, the sodium thiosulphate would gradually change colour, this being rendered evident by the yellowing of the whites.

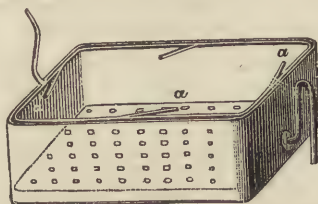


FIG. 71. — WASHING TROUGH.

All papers fixed in hypo must therefore be washed in running water for at least six hours, care being taken that the elimination of the hypo is not impeded by the prints sticking to each other. This operation is usually performed in a vessel such as that shown in fig. 71, in which the inrush of the water keeps the prints in constant motion.

There are many tests enabling unchanged silver salts or hypo to be detected in prints.

Silver sodium thiosulphate is like most other silver compounds at once converted into metallic silver by a so-called alkaline developer after it has been exposed to light, and a knowledge of this fact enables us to ascertain if any traces of this substance, or of unaltered silver chloride or albuminate, remains in the pores of the paper.

To show you how the test is carried out, and also to impress upon you the necessity for leaving the prints for a sufficient length of time in the fixing bath, I have here eight pieces of ordinary albuminised paper, which have been slightly darkened by exposure to light, and then fixed and washed in the ordinary way.

On the back of each piece of paper is written, as you see, the number of minutes during which it remained in the hypo, these being 4, 8, 16, and 32 minutes respectively. The pieces marked B were washed for one hour in running water, those marked G for six hours. Taking first the piece fixed for four minutes, and washed for six hours, and immersing it in ferrous oxalate, you see it blackens all over. Repeating the experiment with the other pieces, we find that the piece which had been eight minutes in the hypo also blackens, but the pieces which had been fixed for sixteen and thirty-two minutes do not blacken.

Now, taking the piece fixed for 32 minutes, and then washed for one hour only, you see that it also blackens, showing that the washing was insufficient.

We may, in fact, conclude from these experiments that under the given conditions the prints should be fixed for at least sixteen minutes, and washed for at least six hours.

In ferrous oxalate we possess the most delicate test for detection of traces of silver salts in the paper, and by applying it in the manner just indicated to a tiny piece torn off the corner of your finished prints, you will at once be able to tell whether they will subsequently fade or not.

Evidently, both the mountant employed to affix the prints to the mounts and the mounts themselves, must be absolutely free from acids, hypo, or indeed from any substance capable of acting upon metallic silver.

The mountant usually employed is thick starch, which has much to recommend it, but care must be taken to make it as required, for starch, like many other organic substances, rapidly becomes acid on exposure to air.

To test for acids in a mount is a very simple matter. To illustrate how the test is carried out, I have here a piece of ordinary grey cardboard. Breaking this up into small pieces, I boil them with a little water, and then filtering the liquid, I add to the filtrate a few drops of phenol phthalein, reddened by the addition of a trace of sodium carbonate, when you see the red liquid becomes almost colourless, showing that an acid is present.

The most delicate test for hypo depends upon the fact that nascent hydrogen will convert this substance into sulphuretted hydrogen, a gas the least trace of which will blacken papers moistened with lead acetate.

To apply the test I break up this piece of white cardboard into small pieces, and boil them up with a little water in a test tube. Now, permitting the whole to cool somewhat, I add to the mixture a fragment of pure zinc, followed by a little hydrochloric acid, placing meanwhile over the mouth of the tube a little piece of blotting paper, moistened with lead acetate, when the gradual blackening of the paper points conclusively to the fact that this sample of cardboard contains hypo, and is quite unfit therefore for mounting prints upon.

#### SUMMARY.

*A loss in density occurs during toning and fixing.*

*Free silver nitrate precipitates gold chloride or chloroplatinic acid.*

*Silver photochloride is decomposed by hypo, becoming converted into soluble sodium thiosulphate.*

*Chloroplatinic acid reduces density more than a so-called alkaline gold toning bath.*

*Hypo is decomposed by most acids.*

*Sulphur and sulphur dioxide, particularly in the nascent state, attack silver.*

*Every print toned removes a certain quantity of precious metal from the toning bath, and every print fixed converts a certain quantity of sodium thiosulphate into silver sodium thiosulphate.*

The rate of toning is influenced by the degree of concentration, the degree of acidity and temperature of the toning bath, and by the quantity of silver photochloride on the print.

Platinum is always deposited black, gold either red, blue, or colours between these.

Rapidly deposited gold is blue, slowly deposited gold red.

Toning baths containing platinum remains in good order until the metal is exhausted.

Toning baths containing gold must, to give dark tones, be strengthened from time to time, and neutralised with sodium carbonate, etc.

Gold toning baths containing sodium carbonate do not require neutralisation.

Hypo slowly attacks metallic silver, i.e., a print containing this substance will slowly fade.

All silver salts become darker in time when in contact with organic matter, i.e., the whites of a print containing such a salt will slowly turn yellow.

All silver salts are, when exposed to light, blackened by potassium ferrous oxalate.

All acids slowly attack silver.

Mountants and mounts must be free from acids and from hypo.

Acids in mounts are detected by phenol-phthalein. Hypo in mounts by the hydrogen and lead paper test.

## LECTURE XXXIII.

ACTION OF LIGHT UPON CERTAIN FERRIC COMPOUNDS—REACTIONS OF FERROUS AND FERRIC COMPOUNDS WITH POTASSIUM FERROCYANIDE, FERRICYANIDE, GALLIC ACID AND POTASSIUM CHLOROPLATINITE—PRINTING-OUT "BLUE" PROCESSES WITH POTASSIUM FERRO AND FERRICYANIDES AS DEVELOPERS—THE "BLACK" GALLIC ACID PROCESS—ACTION OF LIGHT UPON FERRIC OXALATE—THE COLD BATH, HOT BATH, AND PRINTING-OUT PLATINOTYPE PROCESSES—ACTINOMETERS AND THEIR USE—PRECAUTIONS TO BE OBSERVED WITH PAPER CONTAINING POTASSIUM CHLOROPLATINITE.

**S**ALTS of iron as well as salts of silver are acted upon by light, and use is made of this fact in the photographic processes, which will be described in the present lecture.

It will be necessary before proceeding to describe these processes to briefly study certain characteristic properties of the compounds of iron.

Iron exists chiefly in two states of combination, viz., as ferrous and as ferric salts, the latter being derived from the former by oxidation, and conversely, deoxidation converts the latter into the former.

As examples of these two salts, I have here solutions of ferrous and ferric sulphates, and with these compounds I will now make a few experiments.

Taking separate portions of the solution of ferrous sulphate I add to it solutions of gallic acid, of potassium ferrocyanide, and of potassium ferricyanide, and you see that with gallic acid no precipitate is obtained, whilst with potassium ferro and ferricyanides we obtain light and dark blue precipitates.

The light blue precipitate obtained with potassium ferrocyanide consists at first of potassio ferrous ferrocyanide  $K_2Fe_2(Cn)_6$ , but in contact with air it rapidly becomes converted into deep blue ferric ferrocyanide (Prussian blue)  $Fe_4(FeC_6N_6)_3$ .

The dark blue precipitate given with the ferricyanide is ferrous ferricyanide (Turnbull's blue)  $Fe_3Fe_2(Cn)_{12}$ .

Adding now the same reagents to the ferric sulphate, we obtain with the gallic acid a blue-black precipitate, with the ferrocyanide a dark blue precipitate, and with the ferricyanide merely a dark brown colouration. The blue-black precipitate given with the gallic acid is sometimes called ferric gallate, but is probably of indefinite composition. The deep blue precipitate given with the ferrocyanide consists in this case of potassio-ferric ferrocyanide or



soluble Prussian blue,  $K_2Fe_4(CN)_{12}$ , so called from the fact of its being soluble in water.

Adding now potassium chloroplatinite to the ferrous and ferric sulphate you see that with the former metallic platinum is at once precipitated, whilst with the latter no change occurs.

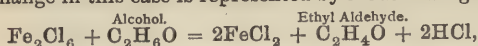
We may tabulate all our results thus:—

	<i>Gallic Acid.</i>	<i>Potassium Ferrocyanide.</i>	<i>Potassium Ferricyanide.</i>	<i>Potassium Chloroplatinite.</i>
Ferrous salts ....	No change.	(Finally) Prussian blue.	Prussian blue.	Precipitate of metallic platinum.
Ferric salts	Blue black precipitate.	Turnbull's blue.	No precipitate.	No change.

Now, ferric salts, particularly when in contact with organic matter, are readily converted by light into ferrous salts, the organic matter being meanwhile oxidised.

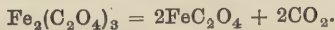
To illustrate this I have here a solution of ferric chloride in alcohol, and adding first some potassium ferricyanide to a portion of it to make sure that no ferrous salt is present, I then expose the remainder for five minutes to the light given out by burning magnesium, after which, as you see, the ferricyanide gives a blue precipitate, showing that some ferrous chloride has been formed.

The change in this case is represented by the following equation:



the dechlorination of the ferric salt being accompanied by the oxidation of the alcohol.

Here again I have pieces of paper coated with potassio-ferric oxalate, and which have been exposed to sunlight beneath a dark cross, when, as you see, a visible change has been produced, the ferric becoming ferrous oxalate, probably in accordance with the equation—



Instead of potassio-ferric oxalate I might have used the tartrate, citrate, or other organic salt of iron, when the change would have been of a similar nature. To illustrate the use made of the gallic acid reaction, I have here a piece of paper coated with a mixture of ferric tartrate and gum arabic, and then exposed to light beneath a positive transparency made from an ordinary steel engraving.

Now you will readily follow me when I say that the portions of the paper under the lines of the transparency will remain coated

with a ferric salt, whilst under the other portions this ferric salt will become converted into a ferrous one.

Floating the paper on a solution of gallic acid, mixed with a little oxalic acid, you see we get a black positive print, the unchanged ferric salt here reacting upon the gallic acid in the usual way.

I have here another piece of paper coated with a mixture of ferric-ammonium citrate, ferric chloride and gum arabic, and then exposed to light beneath the negative of the same engraving whose positive we have just utilised.

Floating this upon a solution of potassium ferrocyanide you see that we obtain a deep blue on a very light blue ground, the unchanged ferric salt beneath the lines of the negative here reacting upon the ferrocyanide and giving Turnbull's blue, whilst the ferrous compound beneath the other portions is practically without action upon the ferrocyanide. To clear the print it is only necessary to place it in 10 per cent. hydrochloric acid, which dissolves away the traces of Prussian blue on the ground of the print without affecting the Turnbull's blue of the lines.

Here is a third piece of paper coated with a mixture of ferric ammonium oxalate and gum arabic, and exposed to light beneath the same negative.

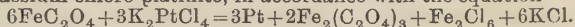
Floating this upon a solution of potassium ferricyanide, we obtain a blue image upon a white ground, the ferrous salt produced under the clear lines of the negative reacting upon the ferricyanide in the usual way, the ferric salt beneath the other portions not being coloured by the ferricyanide.

All these processes are exceedingly useful to engineers and others, to whom it is often a matter of importance to be able to rapidly and cheaply copy a plan, etc. In such a case, if the plan is originally made on tracing paper with very black Indian ink, mixed with a little gamboge, copies can be made very expeditiously in the usual way.

Owing, however, to the great difficulty of rendering the half-tones of a negative properly by these processes, they have not been so generally used for the production of prints from negatives taken direct from nature.

It is far otherwise, however, with the platinotype processes, which, for beauty of results, facility of rendering half-tone and permanency leave nothing to be desired.

The fundamental principle underlying every modification of this process is readily understood, and depends upon the fact that potassio-ferric oxalate becomes converted, in contact with light, into the corresponding ferrous salt, which latter reacts upon potassium chloro-platinite, in accordance with the equation—



Now, since the quantity of ferrous oxalate present upon any portion of the print is proportional to the intensity and to the duration of the light which has acted upon that portion, and since

the quantity of ferrous oxalate present determines the amount of platinum reduced, it follows that with correct exposure beneath a good negative the positive print in platinum should be the direct counterpart of the original.

To illustrate the principle underlying all the platinotype processes, I have here some paper coated with potassio-ferric oxalate and exposed to light beneath a black cross, and floating it on a solution of potassium chloroplatinite mixed with potassium oxalate, you see that the cross comes out white on a black ground of metallic platinum.

Methods of working in platinum may be practically classified into

1. Cold bath development processes.
2. Hot " "
3. Printing out processes. "

To carry out the first process, paper sized with gelatine, arrow-root or algeine is floated on a solution containing ferric oxalate, oxalic acid, and a trace of mercuric chloride, and then dried. After exposure for a sufficient length of time beneath the negative, the image is developed by floating it on a cold solution containing in every ounce 30 grains of potassium oxalate, 30 grains of potassium biphosphate, and 5 grains of potassium chloroplatinite.

I have here an exposed cold bath, platinotype print, and floating it for a few seconds upon the developer, you see that I obtain a beautifully graduated image in platinum black.

The residue of unchanged ferric oxalate has still, however, to be removed. To effect this, I place the print in a dilute solution of hydrochloric acid, which, after some time, will dissolve out every trace of iron salt, and then transferring the print to a second and third bath of the same acid, I finally eliminate the acid itself by washing the print in running water.

Ferric oxalate is itself, as you see by the sample before you, a brownish yellow powder. Placing some of it in this test tube containing water, you see it is insoluble therein, but adding to the mixture a little oxalic acid it at once enters into solution. It is for this reason that oxalic acid is used with the ferric oxalate in coating the paper.

Now, diluting the solution I have just obtained with a considerable bulk of water you perceive that the ferric oxalate is reprecipitated, but adding hydrochloric acid the precipitate redissolves. It is to avoid this, and to remove the unchanged ferric oxalate from the paper, that after development the prints are placed, not in water, but in hydrochloric acid.

Unless care be taken by using at least three baths of this acid to remove every trace of iron from the paper, the whites of the print will be sure to turn yellow in time, for any iron salt in contact with organic matter (in this case the paper itself) will slowly oxidise that organic matter under the influence of light.

Ferrous oxalate is, like the corresponding ferric compound, insoluble in water, but soluble in potassium oxalate, and it is for

this reason that the solution of potassium chloroplatinite is mixed with potassium oxalate. We may, in fact, look upon the potassium oxalate in the developer as dissolving out the ferrous oxalate formed by light, and so enabling the potassium chloroplatinite to act upon it, the solution of the ferrous oxalate and the precipitation of metallic platinum taking place concurrently.

The sodium biphosphate is added in order to give greater purity to the whites, but plain potassium oxalate would develop the image, although not so perfectly.

The advantages of this modification of the platinotype process are that the paper keeps very well, no special precautions being necessary to maintain it dry; ferric oxalate not being a deliquescent substance. Its disadvantages, on the other hand, are that the chloroplatinite is slowly acted upon by the potassium oxalate, for which reason the developer very soon deteriorates; another more serious disadvantage being the great waste of expensive platinum, owing to the comparatively large quantity of chloroplatinite which it is necessary to use in the developer.

In the next process the paper is coated with ferric oxalate, oxalic acid, ferric chlorate, and potassium chloroplatinite, the quantity of the latter taken being such as experience has shown to be necessary for each print and no more.

Evidently in this case the process becomes more economical, for there is little or no waste of platinum.

To develop the print, it is floated upon a slightly acid solution of potassium oxalate, containing 160 grains to the ounce of water, heated to about  $85^{\circ}\text{C}$ , the hot solution being, in this case, necessary to enable the chloroplatinite to react upon the ferrous oxalate. If, however, the exposure is very considerably prolonged, then a cold solution of potassium oxalate may be used.

To illustrate this modification of the platinotype process, I have here two prints, one exposed for about two minutes, the other for thirty minutes, to sunlight, and floating the first upon a hot solution of potassium oxalate, and the second upon a cold solution of the same substance, we obtain, as you see, in both cases an image in metallic platinum.

Immersion in baths of hydrochloric acid completes the prints just as before. Since, in the foregoing processes, the *visible* change produced upon exposure to light is not very well marked, it becomes almost essential to employ, during printing, some kind of actinometer.

You have before you a very useful instrument of the kind introduced by the Autotype Company, of London. It consists, as you see, of a narrow slip of glass of varying actinic opacity capable of being placed over a slip of any material which will change under the influence of light (fig. 72). Under each piece of glass of a uniform tint is a Roman numeral, and as there are twelve tints, so there are twelve numerals.



To use this instrument in platinotype printing, the following solutions are made:—

A.  
Potassium ferrocyanide.. .. 30 grains  
Water .. .. ½ ounce

B.  
Ferric ammonium citrate .. .. 150 grains  
Water .. .. 2 ounces

and mixed together. Paper is then floated upon the mixture for five minutes and rapidly dried.

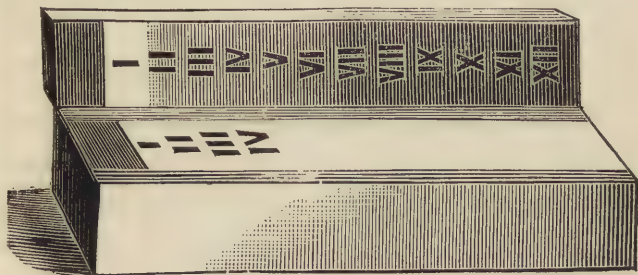


FIG. 72.—THE AUTOTYPE ACTINOMETER.

To use the actinometer a slip of this paper is placed in the instrument, and the whole exposed to the same light as the negative. On looking at the actinometer from time to time, the numbers will be seen to print blue upon the light green ground of the paper, and evidently the higher the number printed, the greater will be the amount of change effected by light.

With a little practise it is easy to classify negatives according to their densities in terms of the actinometer numbers, and in this way platinotype printing may be carried out with ease and certainty. It is almost unnecessary to remind you that the darkening of a *silver* haloid cannot, in any way, measure the amount of change experienced by an *iron* salt.

In the printing-out platinotype process the paper contains potassium chloroplatinite, sodio-ferric oxalate, glycerine, potassium chlorate, mercuric chloride and sodium oxalate.

By holding the paper over a vessel of boiling water just before placing it in contact with the negative, these substances are brought into a state of semi-solution, and are consequently ready to react upon each other, with the result that on exposure to light the image prints out in metallic platinum, and is finished by immersing it in successive baths of hydrochloric acid.

Potassium chloroplatinite being an exceedingly deliquescent substance, all papers containing it must be kept in special recep-

tacles called calcium tubes consisting, as you see, of a tin box made in three parts. The lower parts contain calcium chloride to keep the paper dry, the middle part parts the paper, and the upper part is a lid of the usual form.

#### SUMMARY.

*Ferric salts, particularly if organic or if in contact with organic matter, are converted by light into ferrous salts.*

*Gallic acid gives a blue black precipitate with ferric salts.*

*Potassium ferrocyanide gives a blue precipitate with ferric salts.*

*Potassium ferricyanide gives a blue precipitate with ferrous salts.*

*Potassium chloroplatinite is decomposed by ferrous salts, platinum black being precipitated.*

*Ferrous and ferric oxalates are insoluble in water, but soluble in oxalic acid, in certain oxalates, and in hydrochloric acid.*

*Water decomposes a solution of ferric oxalate in oxalic acid.*

*Potassium oxalate soon reduces solutions containing potassium chloroplatinite.*

*The change produced by light upon ferric salts is not readily perceptible to the eye.*

*An actinometer indicates the extent to which light has acted upon the substance used with it.*

*The silver haloids are altered by light at a rate different to that at which it acts upon ferric oxalate.*

*The rays which act upon ferric oxalate are not the same as those which act upon any silver haloid.*

*The actinometer for platinotype work must be furnished with paper coated not with silver haloid but with an organic ferric salt.*

*Potassium chloroplatinite and calcium chloride are both deliquescent.*

*A calcium tube contains a relatively large quantity of calcium chloride, and so keeps hot bath or printing-out platinotype paper quite dry and in good condition.*

## LECTURE XXXIV.

CHROMIUM COMPOUNDS AND THEIR PHOTOGRAPHIC USES—ACTION OF  
LIGHT UPON MIXTURES OF DICHROMATES AND ALBUMEN, GELATINE  
OR GUM—THE POWDER PROCESS AND ITS USE IN THE PRODUCTION  
OF REVERSED NEGATIVES—PHOTO-VITRIFIED ENAMELS—COLLO-  
GRAPHY—PHOTO-LITHOGRAPHY.

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THE metal chromium combines in several proportions with oxygen to form several oxides, but only two of these are of photographic interest.

Chromic oxide,  $\text{Cr}_2\text{O}_3$  is, as you see by the sample before you, a greenish powder which combines with acids to form salts of chromium such, for instance, as chromium sulphate  $\text{Cr}_2\text{O}_3 \cdot 3\text{SO}_3$ , or as it is more usually written  $\text{Cr}_2(\text{SO}_4)_3$  a substance occurring when pure as a deep green solid, and in combination with potassium sulphate as the purplish red solid chrome alum.

Chromic anhydride,  $\text{CrO}_3$ , is, on the other hand, a crimson, extremely deliquescent, crystalline, solid, differing completely from chromic oxide,  $\text{Cr}_2\text{O}_3$ , in not combining with acids to form salts of chromium, but, on the contrary, combining with bases to form chromates and dichromates.

Thus, for instance, this yellow solid is potassium chromate, the formula for which might be written  $\text{K}_2\text{O} \cdot \text{CrO}_3$ , and this red solid potassium dichromate, the formula for which we might similarly express as  $\text{K}_2\text{O} \cdot 2\text{CrO}_3$ .

One of the chief characteristics of chromic-anhydride is its tendency to oxidise any substance with which it is brought into contact, becoming itself converted into chromic oxide. Placing some of it upon this plate, I drop a little alcohol upon the crystals, when as you see, considerable heat is evolved and a greenish residue of chromic oxide remains. The alcohol has in this case been oxidised to ethyl-aldehyde, and the entire change might be expressed by the equation—



In a minor degree this property is shared by the chromates and dichromates, particularly by the latter.

Now, certain organic substances such as paper, albumen or gelatine, are oxidised by potassium or ammonium dichromate, the action being greatly facilitated by light.

Here I have a sheet of paper which has been steeped in a solution of potassium dichromate, then dried and exposed to light

beneath a black cross, when, as you see, the cross has printed out yellowish-red upon a brownish ground. The cellulose of the paper has here been oxidised by the dichromate, the visible image being either a mixture of green chromic oxide with the oxidation product of the cellulose, or possibly a compound formed by their union.

Albumen and gelatine yield upon oxidation products which are insoluble in water.

To prove this I have here a solution containing gelatine, and adding a little chlorine water to it, you see that I obtain a whitish precipitate. The exact composition of this substance is not known, but it is certain that it consists mainly of oxidised gelatine in combination probably with chlorine.

I have here a sheet of paper which has been coated with a mixture of gelatine and potassium dichromate, then dried and exposed to light beneath the black cross, and placing it in warm water you perceive that the unchanged gelatine and dichromate gradually dissolve out, leaving on the paper the mixture of oxidised gelatine and chromic oxide.

Albumen, gelatine, and gum arabic are more or less sticky in their unchanged condition, this being probably due to their slightly hygroscopic nature, but exposed to light, mixed with a dichromate, this stickiness is to a great extent removed.

These facts form the starting points of a large number of processes, which we may classify as follows:—

1. Processes depending upon the partial removal of the natural stickiness of albumen, gum arabic, gelatine, etc., when exposed to light mixed with certain dichromates.
2. Processes depending upon the partial insolubility of gelatine, etc., when exposed to light under similar conditions.

I will begin by illustrating two processes coming under the first heading.

In this printing frame there is a sheet of ordinary albuminised paper, which has been floated wrong side down, upon a saturated solution of potassium dichromate, then dried and exposed beneath a line positive in the usual way, the side not albuminised facing the film. This paper I now place in water rendered slightly alkaline with ammonia, when, as you will readily understand, most water will be absorbed by those portions where light has not acted, *i e.*, the dense lines of the positive, and least where light has acted most strongly. Now placing the print for a minute or so between two sheets of blotting paper so as to remove the excess of water, I next dust a little very fine electrotype plumbago over the surface and gently rub it in with a pad of cotton wool, when, as you see, the powder adheres to the lines only, and so enables one to obtain a copy of the original in plumbago.

Of course, if instead of having, during printing, placed the wrong side of the paper in contact with the positive, I had placed the albuminised side in contact, I should then have obtained a reversed positive.



A similar process enables reversed negatives to be very readily made. The glass plate in this printing frame has been coated with the following mixture—

Gum arabic	..	..	..	..	24 grains
Glucose	..	..	..	..	48 "
Sugar candy	..	..	..	..	10 "
Water	..	..	..	..	1 ounce
Saturated solution of ammonium di- chromate	..	..	..	..	100 minims

just as if collodion were being used, and the water having been driven off by a gentle heat, the plate has been exposed to light behind a negative in the usual way.

Dusting some plumbago on the plate I work it round and round with this soft brush when, as you see, the plumbago adheres to the lines and so enables me to develop up a counterpart of the original necessarily reversed since both films were in contact.

To complete the process, I coat the developed film with plain collodion and let this set, and then remove the excess of dichromate by washing it in water. Evidently, if instead of using a negative I had employed a positive, I should have obtained a counterpart of the original, and the process affords a ready means of multiplying transparencies, lantern slides, etc., the negatives of which we do not possess. Reversal is, in this case, of no moment, since on covering each slide, etc., with glass in the usual way, we can take care to so turn the finished result, when placing the whole in position, that the image will appear non-reversed.

The same process is a very valuable means of making photographic burnt-in enamels. In this case a reversed positive is made use of, and the surface about to receive the enamel is coated with the mixture of gum, dichromate, &c. After exposure to light this surface is then dusted over, not with plumbago, but with a suitable powder, which will melt under the action of heat, the image being developed up just as before. Development finished the whole is coated with collodion, the excess of dichromate washed out and the plate then intensely heated in a suitable furnace until the enamel begins to melt, next covered over with glaze and again heated, when the picture becomes burnt in, and is thereby rendered practically indestructible.

You remember, of course, that the reason why the powder used adheres in such cases to certain portions of the print and not to others, is due to the fact that those portions which have been exposed to light lose, to a greater or lesser extent, their affinity for water.

Let us suppose, for example, that we expose a film of gelatine and dichromate to light, and then wet it, the powder would naturally adhere in greatest quantity to those portions which have been most wetted, *i.e.*, to those portions which had received the least exposure.

But if, on the other hand, instead of applying a powder to the exposed and wetted surface, we passed over it a roller charged with greasy black ink, then this ink would naturally adhere to those portions which had been least wetted, *i.e.*, to those portions which had received the most exposure.

Using, in fact, a powder, we get a positive from a positive, or a negative from a negative, but a greasy ink gives us a positive from a negative for the reason just laid down.

To illustrate this fundamental difference I have here a second print made by the process first described, and which would, if developed with plumbago yield a positive, and now placing it upon this glass plate I gently roll over the surface a gelatine roller covered with greasy and rather thin printers' ink, when you see that the ink does not adhere to the lines, but to the ground, giving us a negative impression.

Now, placing over the print a sheet of clean paper, and gently pressing the two in contact, the paper removes some of the ink, and so enables me to obtain another negative. By again applying the roller, followed by another sheet of paper, I could in this way obtain a very large number of impressions, and evidently, if instead of having used a positive, I had employed a negative, these impressions would be themselves positives.

An ordinary negative would, however, be unsuitable, owing to the fact that although what I might call the original positive is non-reversed, the impressions taken from it in the manner indicated would necessarily be themselves reversed. It is essential, therefore, to employ originally a reversed negative.

A process of this sort is said to be photo-mechanical, since photography is only concerned in the production of a part of the work, the other portions being done by different, and, as we should say, purely mechanical operations.

As illustrating another of these photo-mechanical processes, I will describe the production of collotypes, or collographs as they should be more properly called, a large collection of which you see upon the table.

A perfectly flat and rather stout glass plate being taken, its four edges are rounded off, and its surface is then finely ground with emery powder.

The plate having been very carefully cleaned, its ground surface is covered with a thin layer of a substratum, made by mixing 20 parts of beer with one part of syrupy potassium silicate, and the whole dried by artificial heat. The object of this substratum is to prevent the film of gelatine from separating from the glass during subsequent operations.

The next operation consists in very accurately levelling the glass plate, then placing it for a minute in water rendered slightly alkaline with ammonia, replacing it on the levelling slab, and at once coating it with the following mixture, maintained at 50° C by means of a hot water bath:—

Collographic gelatine	..	..	250 grains
Potassium dichromate	..	..	50 "
Water .. .. .	..	..	7 ounces
Strongest ammonia.	..	..	16 minims

using about eight minims for every square inch of surface. When the coating has set the plate is then transferred to a drying box like that already figured, and dried at a fixed temperature of 45° C.

The plate is then exposed beneath a negative for a suitable length of time, after which the film side of the exposed plate is placed over a sheet of black paper, and the reverse side of the glass, which must be perfectly clean, is then exposed to light for about half the time the negative took to print, in order to render quite insoluble the layer of gelatine next the glass.

The plate is then washed in running water until every trace of bichromate has been removed, and next placed in the following solution :—

Water	..	..	..	..	2 ounces
Glycerine	..	..	..	..	4 "
Common salt	..	..	..	..	65 grains
Strongest ammonia	..	..	..	..	45 minims.

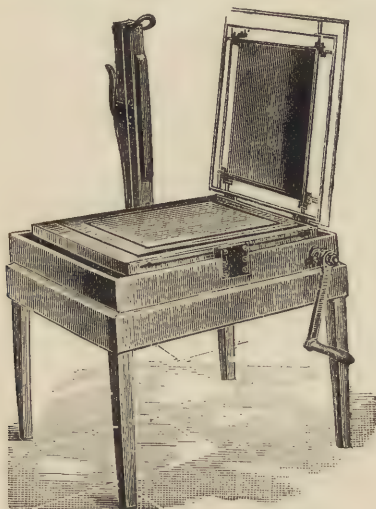


FIG. 73.—COLLOGRAPHIC PRESS.

until the relief due to the unequal expansion of the gelatine has almost disappeared, after which the excess of liquid is removed

with a clean rag, and then rolled up with a gelatine roller covered with collographic ink.

The plate is then placed in a truly vertical position in a collographic press (fig. 73), a sheet of suitable paper placed over the whole, and the proofs pulled in the usual way.

A somewhat similar process is made use of to obtain photolithographs. To understand this I must begin by explaining the fundamental principles of lithography itself.

A drawing, etc., having been made upon paper with a pencil consisting essentially of a kind of hard soap, the paper is pressed in contact with a lithographic stone.

The paper having been removed, gum water mixed with a little nitric acid is poured over the stone, when the soap constituting the drawing, etc., left upon the stone is decomposed by the nitric acid, the fatty acids of the soap combining with the calcium of the stone to form insoluble calcium salts, these protecting the portions of the stone beneath them from further action. Upon the other portions of the stone the acid can, however, act, with the result that these portions are rendered more porous than before.

If a roller charged with fatty ink is now passed over the whole, it is evident that the ink will adhere only to those portions upon which the drawing was impressed, and by now placing a sheet of paper over the stone, and passing the whole through a suitable press, some of the fatty ink will come off upon the paper, leaving upon the latter a copy of the original.

To illustrate the first step in the production of a photo-lithograph, I have in this frame a print made from a reversed negative upon a piece of stout paper, coated with a 10 per cent. solution of gelatine, and then sensitised by being floated on a 3 per cent. solution of potassium dichromate.

Removing the print, I pass over it a roller charged with special ink, and then placing the whole in water at 50°C, I gently rub the black coating with a pad of cotton wool when, as you see, the gelatine remaining soluble under the ground carries away the ink with it, but the latter obstinately adheres to the lines.

It only remains to dry this transfer, as it is called, then press it in contact with a lithographic stone, and proceed exactly as before, the greasy ink here playing the part of the soap pencil in lithography proper.

#### SUMMARY.

Chromic anhydride or its salts, the *dichromates*, tend to oxidise organic matter, particularly in light.

The oxidation products of albumen and gelatine are insoluble in water.

Oxidised gum Arabic, gelatine and albumen are less tacky than the original substances.

A powder like plumbago adheres energetically to surfaces containing gum, albumen, etc., but not at all to surfaces containing



these substances mixed with a *dichromate* and *exposed* for sufficiently long to *light*.

The degree to which the *plumbago*, etc., adheres *varies inversely* as the extent of the action produced by *light*.

A *photo-vitrified enamel* is a *positive* in enamel powder burnt in on porcelain, etc.

A *greasy ink* adheres energetically to surfaces containing *gelatine*, *albumen*, etc., which have been *exposed* for a sufficient length of time to *light*, but not at all to those surfaces in their *original* state and *wet*.

Water readily wets surfaces of *unchanged gelatine*, *gum*, &c., but does not wet such surfaces if they have been *exposed to light*.

A *collograph* (collo type) is a *print in fatty ink* of any colour adhering to a *gelatine surface*.

A *lithographic stone* is attacked by *nitric acid* and rendered porous where *unprotected*, but remains *unattacked* where covered with a *drawing in soap* (litho-pencil) or in *fatty ink* (photo-litho transfer).

A *lithographic stone* will, if sufficiently porous, be incapable of being greased by *fatty ink*.

*Photo-mechanical* processes are those in which *photography* performs only a *portion* of the work, the *prints* themselves being made by methods other than *photographic* (collography, photo-lithography).

## LECTURE XXXV.

PROCESSES DEPENDENT UPON THE INSOLUBILITY OF DICHROMATED GELATINE WHICH HAS BEEN EXPOSED TO LIGHT—THE AUTOTYPE OR CARBON PROCESSES—NECESSITY FOR REVERSED NEGATIVES—SINGLE AND DOUBLE TRANSFER—ENAMELLED CARBON PRINTS—METHODS OF OBTAINING GELATINE RELIEFS—THE WOODBURYTYPE PROCESS—ACTINOMETER FOR USE IN PROCESSES IN WHICH THE DICHROMATES ARE EMPLOYED.

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WE have in this lecture to consider certain other processes depending upon the fact that a film of dichromated gelatine is rendered more or less insoluble when exposed to light beneath, say, a negative.

It is evident, in the first instance, that if a pigment be mixed with the dichromated film, and the whole treated with warm water after exposure to light, the gelatine, in dissolving away more or less will carry the pigment with it.

To illustrate this, I have here a film of gelatine, Indian ink, and potassium dichromate, spread upon paper and exposed to light beneath a black cross. Placing the whole in warm water, you see that the gelatine under the cross remains insoluble, but dissolves everywhere else, carrying the Indian ink with it, the result being a white cross, formed by the bare paper upon a black ground formed of the mixture of insoluble gelatine and Indian ink.

Clearly, any negative, say a copy of an engraving in which the half tones are obtained by lines or by dots, could be used to obtain a pigment print in the manner just indicated, this pigment print being, in fact, nothing else than a photo-litho transfer not inked up, and made with gelatine mixed with a pigment instead of with plain gelatine, and it is also evident that any pigment which did not itself act upon the gelatine or the dichromate might be used instead of the Indian ink.

If however we attempt to make a print in this way from an ordinary negative taken direct from nature we find it is practically impossible to get a good result for the following reasons.

The high lights of such a negative are, we remember, represented by a high degree of opacity, the deep shadows by relatively clear glass, and the half tones by deposits of varying opacities. Now in the counterpart of this, the gelatine beneath the high lights would have to remain completely soluble, that beneath the deepest shadows being rendered completely insoluble, and the degree of insolubility of the gelatine beneath any half tone being the reciprocal of the opacity of that half tone.

Doubtless with a correct exposure this is what actually occurs, but the difficulty arises when we attempt to dissolve away the gelatine so as to get layers of pigment of varying thickness, for evidently the *whole* of the surface layer of gelatine beneath the shadows and half tones will have been rendered insoluble, and will consequently prevent the gelatine beneath from being dissolved away. The process as thus carried out is, therefore, incapable of giving a print from an ordinary negative, although quite capable of giving one from the negative of an engraving, etc.

Evidently, however, if by any means we could dissolve away the gelatine not from that side of it which had been in contact with the negative, but from the other side, then, since the whole of that surface has remained soluble, there would be no skin of insoluble gelatine to interfere with the action of the warm water, and since the depth to which the gelatine has been rendered insoluble depends upon the depth to which the action produced by light has penetrated, it would be possible to obtain a print in pigment the true counterpart of the original.

The process carried out according to the principles just laid down constitutes the so-called carbon process by single transfer.

The following formula may be made use of to prepare the gelatine surface :—

Nelson's No. 1 gelatine	..	..	400 grains.
Amber gelatine	..	..	3000 "
Sugar candy	..	..	460 "
Dry Castille soap in powder	..	..	400 "
Water	..	..	22 ounces.

With the addition of sufficient colouring matter (say about 100 grains for the above proportion) to give the requisite depth of colour.

The colouring matters used are the following:—

*Portrait brown.*—Indian red, 10 parts; Chinese ink, 8 parts; carmine lake, 6 parts.

*Chocolate brown.*—Chinese ink, 3 parts; hydrated peroxide of iron, 2 parts; alizarine dissolved in caustic soda,  $\frac{1}{2}$  part; purpurine,  $\frac{1}{2}$  part.

*Dark brown.*—Indigo,  $2\frac{1}{2}$  parts; Indian red, 6 parts; Vandyke brown, 4 parts; carmine lake,  $1\frac{1}{2}$  parts; lampblack, 30 parts.

*Red brown.*—Chinese ink, 6 parts; carmine lake, 8 parts; Vandyke brown, 8 parts.

*Sepia.*—Lampblack, 4 parts; Cologne sepia, 35 parts.

*Warm black.*—Lampblack, 6 parts; carmine lake, 6 parts; burnt umber, 4 parts; indigo, 2 parts.

*Engraving black.*—Lampblack, 38 parts; carmine lake, 4 parts; indigo, 2 parts.

To prepare the mixture, the soap and sugar are first dissolved in the water and the cold solution poured over the gelatine. When this has swelled the whole is heated to dissolve the gelatine and the colouring matter having been added, the mixture is filtered through

flannel and the paper coated with it by special machinery, thoroughly dried and sensitised by plunging it for three minutes beneath the surface of a solution of dichromate made up as follows:

Potassium dichromate	.. ..	62 grains.
Ammonium carbonate	.. ..	3 "
Water	.. ..	7 ounces.

To illustrate the sensitising of the paper, I have here a piece of tissue, as the coated paper is called, and plunging it for three minutes beneath the surface of the solution, I then remove it, and placing the prepared surface upon a sheet of glass, I squeegee out the excess of sensitising solution, a precaution which is absolutely necessary to ensure good results. The paper being sensitised, is placed in a current of air to dry, which it does in about 12 hours or less.

On a large scale, instead of sensitising the tissue separately, the dichromate is mixed with the gelatine in the first instance.

Curiously enough, the moist paper is absolutely insensitive to light, for which reason sensitising can be performed in ordinary daylight, but as the paper becomes sensitive as it dries, the drying must be done in the dark.

Negatives intended for printing in carbon must be either vignetted or printed in a mask, for reasons which will be apparent in a moment.

I have here a negative in contact with a piece of tissue, the whole having been exposed to light, and you will observe that between the tissue and the negative there is a narrow mask of red paper.

Removing the exposed tissue, I soak it in cold water until limp, and then squeegee it in contact with the ground surface of this perfectly clean opal plate. Leaving both in contact for a few minutes, I then place the opal and the tissue in water heated to 40° C. In a few moments, as you perceive, the gelatine at the edges and which has remained soluble begins to ooze out between the tissue and the glass, and when this occurs I lift one corner of the paper and readily pull it off, leaving upon the glass plate what looks like an ugly smear of coloured gelatine. Gently laving this with the warm water, the soluble gelatine is washed away, the final result being a positive in pigment on the opal glass. The object of the mask in this case is to ensure the adhesion of the soluble edges of the print to the support, and so prevent the image itself from being stripped off when the paper is removed.

To prepare a print upon a paper support I have in this dish, containing a dilute solution of alum, a piece of paper coated with gelatine, and first washing away the alum by placing the paper under running water for a minute or so, I then immerse another piece of exposed tissue in cold water until limp, next squeegee it in contact with the paper, and then proceed just as before.

I will now illustrate the preparation of a transparency by this process. I have here a glass plate coated with a thin layer of



gelatine containing a little alum, and using it just as I did the opal I obtain as you see a positive by transmitted light.

All the preceding positives were reversed. This was immaterial so far as the transparency was concerned, but in the case of positives by reflected light it is, of course, highly objectionable.

By employing a reversed negative, we can get what is required at one operation, but, fortunately, there are other means at hand to enable ordinary non-reversed negatives to be utilised, and the process by which this is effected is called "double transfer." The principle involved is simple and depends upon the fact that the image can be developed upon a "temporary" support, say waxed glass or a special kind of paper, and then removed from this support by permitting the developed image to dry in contact with gelatinized paper, and separating the two when this paper is perfectly dry.

To illustrate the process of double transfer, I have here a perfectly clean glass plate, and upon this I pour a solution of three grains of yellow wax in one ounce of benzole, just as if I was collodionising, and, letting the whole stand for a few minutes, I then place it in water and develop a print upon this support in the ordinary way. Meanwhile, pieces of gelatinized paper have been steeping in the alum in this dish, and taking out one of these pieces, I squeegee it in contact with the print upon the waxed glass.

I have here a waxed glass plate carrying the image, and upon which a piece of gelatinized paper has been squeegeed and then permitted to dry, and as you see I can readily pull off the paper, carrying with it the non-reversed print.

Instead of employing glass which had been waxed merely I might have coated it with plain collodion made rather thick, and developed the image upon this basis, when I should obtain on stripping an enamelled positive.

Paper itself can be used as temporary support if care be taken to impregnate it with shellac, and so render it practically impervious to water.

You must have noticed that in every case where dichromated gelatine was employed a certain amount of relief was obtained, due, evidently, to the greater solubility of the gelatine at certain portions.

Here, for instance, is a thick film of bichromated gelatine on paper exposed to light beneath a black cross, and on soaking it in warm water, you see that we obtain the cross itself in relief upon a sunk in ground. If this relief were dried, it would be quite possible to force it into a plate of lead, when, of course, the cross would now be sunk in and the ground raised. On pouring into what we might call the metal mould a quantity of gelatine, mixed with colouring matter, just sufficient to fill the hollow representing the cross, then placing a sheet of white paper over the whole, and removing the paper when the gelatine had set, the paper would take up the layer of pigmented gelatine, and we should obtain in this way a counterpart of the original.

You will now, I am sure, experience no difficulty in understanding the Woodburytype process, numerous specimens of which are on the table before you.

The first thing is to prepare a very thick dichromated gelatine film by covering collodionised glass with gelatine dissolved in five times its weight of water, mixed with ammonium dichromate, sugar and glycerine. Drying by artificial heat would, in this case, be out of the question, so use is made of the hygroscopic properties of calcium chloride, the gelatinised glass plates being placed in boxes containing this substance.

When dry the skin, as the dichromated gelatine is called, is stripped from the glass, and exposed under a reversed negative, the collodionised side of the gelatine facing the film of the latter.

Exposure over a rather thick solution of caoutchouc in benzine is spread over glass, and the exposed film placed in contact with it, collodionised side next the glass, an indiarubber roller being employed to force the surfaces in contact.

When they adhere the whole is placed in warm water, developed in the ordinary way, dried, and again stripped from the glass.

The skin carrying the relief, such as the one I show you, is then placed upon a leaden plate, and a steel plate having been placed over the relief, the whole is forcibly compressed in a

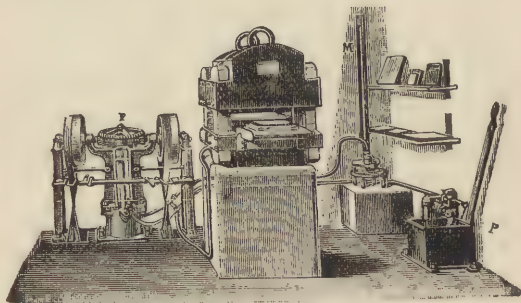


FIG. 74.—HYDRAULIC PRESS FOR MAKING WOODBURY MOULD.

powerful hydraulic press (fig. 74), with the result that a leaden mould of the original is obtained.

This mould is next greased, placed in a special press capable of giving a perfectly even downward pressure, and sufficient gelatine mixed with colouring matter having been poured over it, a sheet of specially prepared paper is placed over the whole and the top of the press brought down, when the excess of ink oozes out at the sides, and an exact copy of the original results, to complete which

it is only necessary to harden it in alum, and then get rid of the alum by placing the prints for some time in running water (fig. 75).

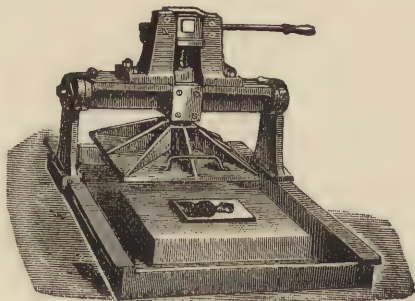


FIG. 75.—WOODBURYTYPE PRESS.

An actinometer is, of course, absolutely necessary in all these processes, and may be of the form already described, but furnished with gelatinised paper sensitised in a five per cent. solution of ammonium dichromate, the numbers then printing dark brown on a light yellow ground.

#### SUMMARY.

The presence of certain pigments in *dichromated gelatine* will not interfere with the action of light upon it.

Paper coated with pigment, gelatine and dichromate can be employed to obtain prints from negatives of line, stipple or dot subjects, but not from negatives direct from nature unless a special method of development is resorted to.

The front surface of a film of dichromated gelatine is rendered insoluble under the deep shadows, as well as under the half-tones, the film of insoluble gelatine on the surface protecting the under portions.

To make pigment prints from negatives direct from nature, the gelatine must be dissolved away from the back.

So-called carbon tissue contains gelatine, pigment, potassium dichromate, and certain other substances.

The pigment used may be of any nature, provided it does not itself act upon the gelatine.

Negatives for carbon printing must be provided with a safe edge, to insure the adhesion of the front surface of the exposed film to the support.

With reversed negatives, prints may be made by single transfer, i.e., direct upon paper, glass, &c.

With non-reversed negatives the prints are themselves reversed ;

to get *non-reversed prints*, use must be made of the *double transfer* process.

In the *double transfer* process the print is first made upon a *temporary support* of glass, paper, &c., and then *transferred* from this to the *final support*.

A *thick film* of *gelatine* and *dichromate* *exposed* beneath a negative and *developed* in warm water from the *opposite side* gives a *gelatine relief* in which the *shadows* are represented by *hills* and the *lights* by the *hollows*.

This *relief* forced into a *lead plate* gives a *mould* in which the *shadows* are represented by *hollows* and the *lights* by *hills*.

*Gelatine*, mixed with *pigment*, poured into this *lead mould* will give a *pigment print* the exact *counterpart* of the *original*.

*Actinometers* for use in processes involving the action of light upon *dichromates* mixed with organic matter should be charged with *gelatinised paper* sensitised in *ammonium dichromate*.



## QUESTIONS FOR SELF-EXAMINATION.

- 1.—What is the luminiferous ether?
- 2.—Draw a figure representing (a) longitudinal, (b) transversal vibrations.
- 3.—Describe and explain the effect of passing a gradually increasing current of electricity through a fine platinum wire.
- 4.—How would you perform the prismatic analysis of white light?
- 5.—What difference would be observed on looking through a prism at a solid, at a dull red heat, and white heat respectively?
- 6.—What is meant by the velocity, length and amplitude of a wave?
- 7.—What are Fraunhofer's lines?
- 8.—Draw the curves of sensitiveness of the silver haloids, and explain how they have been arrived at.
- 9.—Why do we use red light for dark room illumination?
- 10.—What is meant by the disc of confusion?
- 11.—What are the advantages and disadvantages of pinhole photography?
- 12.—What is the law of inverse squares, and how would you prove it true for light?
- 13.—A lamp six feet distant gives a correctly-exposed contact print. What would be the duration of the exposure if the lamp was nine feet from the print?
- 14.—A lens with a stop one inch in diameter gives a correctly-exposed negative of a distant view when uncapped for one second. How long should it remain uncapped if the stop was reduced to  $\frac{1}{2}$  inch?
- 15.—What is a photometer? Can such an instrument give any idea of the actinic powers of two sources of light?
- 16.—What is a reversed negative, and how is it made?
- 17.—Upon what does "halation" depend? Is backing a plate an absolute safeguard against its occurrence?
- 18.—Why is the interior of a camera painted dead black?
- 19.—What is meant by the statement that the index of refraction of a certain sample of glass is 1.642?
- 20.—Why are compound photographic lenses cemented together?
- 21.—One half of a negative is denser than the other. Show by a sketch how you would place the printing frame with respect to the light so as to get an even print.
- 22.—Where should an orthochromatic colour screen be placed, and why?
- 23.—What is meant by the dispersion of a given sample of glass?
- 24.—Sketch an achromatic prism.

- 25.—Sketch a lens free from spherical and chromatic aberration.
- 26.—Why is it necessary to use two different kinds of glass in compound photographic lenses?
- 27.—What would be the effect of taking a picture with a non-achromatic lens?
- 28.—What are the nodal points in a lens? Sketch their position in a lens of the meniscus form.
- 29.—A lens has a principal focus of nine inches, and an object is placed seventy-one inches from its nodal point of admission. At what distance from the nodal point of emission must the ground glass be placed? Assuming the object to be three feet high, what will be the size of the image?
- 30.—A single lens with a half-inch stop just covers a whole plate. Will it still cover a whole plate when the stop is reduced to  $\frac{1}{32}$  inch? Give reasons for your answer.
- 31.—What is curvature of the field?
- 32.—Explain the influence of the position of the stop upon distortion.
- 33.—What are the uses of the vertical swing back?
- 34.—Why has a portrait lens used full aperture so little depth of definition?
- 35.—What is meant by the "field of visibility" of a lens, and what by its "field of definition"?
- 36.—Can a quarter-plate photograph be as truthful a representation of nature as one  $16 \times 12$  inches? Give reasons for your answer.
- 37.—What weight of silver nitrate can be obtained from an old coin weighing 271 grains and containing 75 per cent. of silver?
- 38.—What weight of metallic silver will 404 grains of silver nitrate yield?
- 39.—What weight of silver chloride will 42 grains of silver nitrate yield?
- 40.—How is the amount of energy necessary to decompose a chemical compound measured?
- 41.—In what way does a rise in temperature facilitate the interaction of two substances?
- 42.—What is meant by the statement that certain substances occur in different allotropic forms?
- 43.—Why does silver chloride blacken more readily when exposed to light beneath the surface of silver nitrate than it does under water?
- 44.—Write the formulæ for silver chloride, sub-chloride, oxy-chloride, and photo-chloride.
- 45.—Write a short account of the phenomenon of reversal.
- 46.—What reasons are there for regarding the nature of the change brought about in silver bromide by a very short exposure to actinic light as different in kind from the change brought about by a prolonged exposure?

47.—Write an account of the allotropes of silver bromide, and explain how they are made.

48.—What is the effect of heat upon the allotrope of silver bromide least sensitive to light?

49.—How would you convert a florin into silver nitrate?

50.—How would you make silver nitrate from the silver contained in an old fixing bath?

51.—Describe and explain the effect of adding common salt to (a) silver nitrate, (b) an old cyanide fixing bath.

52.—How would you dehydrate a sample of spirits of wine?

53.—Describe the manufacture of photographic pyroxyline.

54.—How would you select a sample of gelatine suitable for making dry plates?

55.—What takes place when a collodion film containing cadmium iodide is placed in a strong solution of silver nitrate?

56.—For what purpose is (a) plain iodised, (b) bromo-iodised collodion respectively used?

57.—What is the cause of pinholes in collodion negatives?

58.—Explain the action of the preservative in dry collodion processes.

59.—What occurs when a film containing silver iodide is forcibly compressed, and why?

60.—How would you free an old silver bath from ether-alcohol and excess of silver iodide?

61.—Describe the preparation of a collodion emulsion.

62.—Explain the "ripening" of an emulsion.

63.—How would you "cure" a collodion emulsion giving foggy pictures?

64.—What essential difference in the adjustment of the proportions of certain ingredients is there between a collodion and a gelatine emulsion?

65.—Is it possible to make a collodion emulsion as sensitive as a gelatine one?

66.—Can emulsions be made in actinic light, and if so, how, and why?

67.—Can the luminosity of colours be accurately reproduced by photography?

68.—In what way does erythrosin act in increasing the sensitiveness of silver bromide to certain portions of the spectrum?

69.—Describe how you would photograph a view in which white, grey, light blue and dark red occurred.

70.—Explain the use of ferrous sulphate, acetic acid and alcohol in the development of a wet plate.

71.—Why is it that a wet plate developer containing a large quantity of acid gives more contrast than one containing less acid?

72.—Describe and explain what happens when a clean glass plate, upon which a word has been traced with a blacklead pencil, is placed in a mixture of acidified ferrous sulphate and silver nitrate.

73.—How would you develop a gelatino-bromide plate exposed upon a landscape in which there are violent contrasts of light and shade, so as to get a negative devoid of excessive contrast?

74.—What is the difference between a physical and a chemical restrainer in a developer? Give examples of each.

75.—What alteration in the composition of the ferrous oxalate developer is found after plates have been developed in it?

76.—Give your ideas as to the truth or the reverse of the gradations of light and shade as rendered by photography.

77.—During development, how can you distinguish between a properly exposed, an under-exposed, and an over-exposed gelatino-bromide plate?

78.—How does a small quantity of hypo act when added to the ferrous oxalate developer?

79.—What occurs when a silver haloid is added to hypo? It is usually said to dissolve. Is this really the case?

80.—A gelatine negative is found to be too dense. How would you reduce it so as to leave the gradations unaltered?

81.—Discuss the respective advantages and disadvantages of hypo and cyanide as fixing agents for collodion negatives.

82.—What occurs when a negative is intensified with mercuric chloride followed by ammonia?

83.—How would you proceed to intensify a gelatino-bromide negative so as to leave its gradations unaltered?

84.—In copying a line engraving by the wet collodion process: First, what strength of bath? Second, what developer? Third, what intensifier would you use?

85.—Give a detailed account of the method you would adopt to make a wet collodion lantern slide from a whole-plate negative.

86.—Describe how you would make a six diameter enlargement from a quarter-plate negative.

87.—It is required to enlarge a half-inch vignettted head to life size, what process would you adopt for choice, and why? Your object should be to obtain a result as free from granularity as possible.

88.—A print upon sensitised albuminised paper when placed in spring water renders the latter milky. Why is this?

89.—In the gelatino-chloride printing out process an organic salt of silver is present. What purpose does it serve?

90.—Describe and explain the preparation of "preserved" ready-sensitised paper.

91.—What weight of gold trichloride can be obtained from a sovereign weighing 124 grains and containing 91.67 per cent. of gold?

92.—Describe a method of toning developed bromide prints with platinum, and explain the chemical changes produced in the film.

93.—What difference is there in composition between a developed and a printed-out image obtained from silver chloride?



94.—Why are such substances as sodium carbonate or borax added to a toning bath for prints upon albuminised paper?

95.—Describe a method of toning printed-out images on so-called plain paper with platinum, and explain the chemical changes produced.

96.—What special precautions have to be observed in fixing paper prints? Describe and explain a method of testing such prints for (1) unchanged silver salts, (2) hypo.

97.—Compare a developed gelatino-bromide print with a platinotype as regards (1) ease of production, (2) colour, (3) permanency.

98.—Describe the production of a hot bath platinotype print, the coated paper being supplied. State clearly the reasons for each operation.

99.—How can a blue print be made from a negative?

100.—What is a litho transfer? Describe how you would proceed to make one from a line engraving by photography.

101.—Describe the production of a reversed negative by the powder process.

102.—How would you make a collographic printing plate from a negative taken direct from nature?

103.—Describe the preparation of a double transfer carbon print on collodionised glass.

104.—Write an account of the Woodburytype process.

105.—Describe an actinometer for use in printing. With what material would you charge it for use in (1) platinotype work, (2) carbon work, and why?

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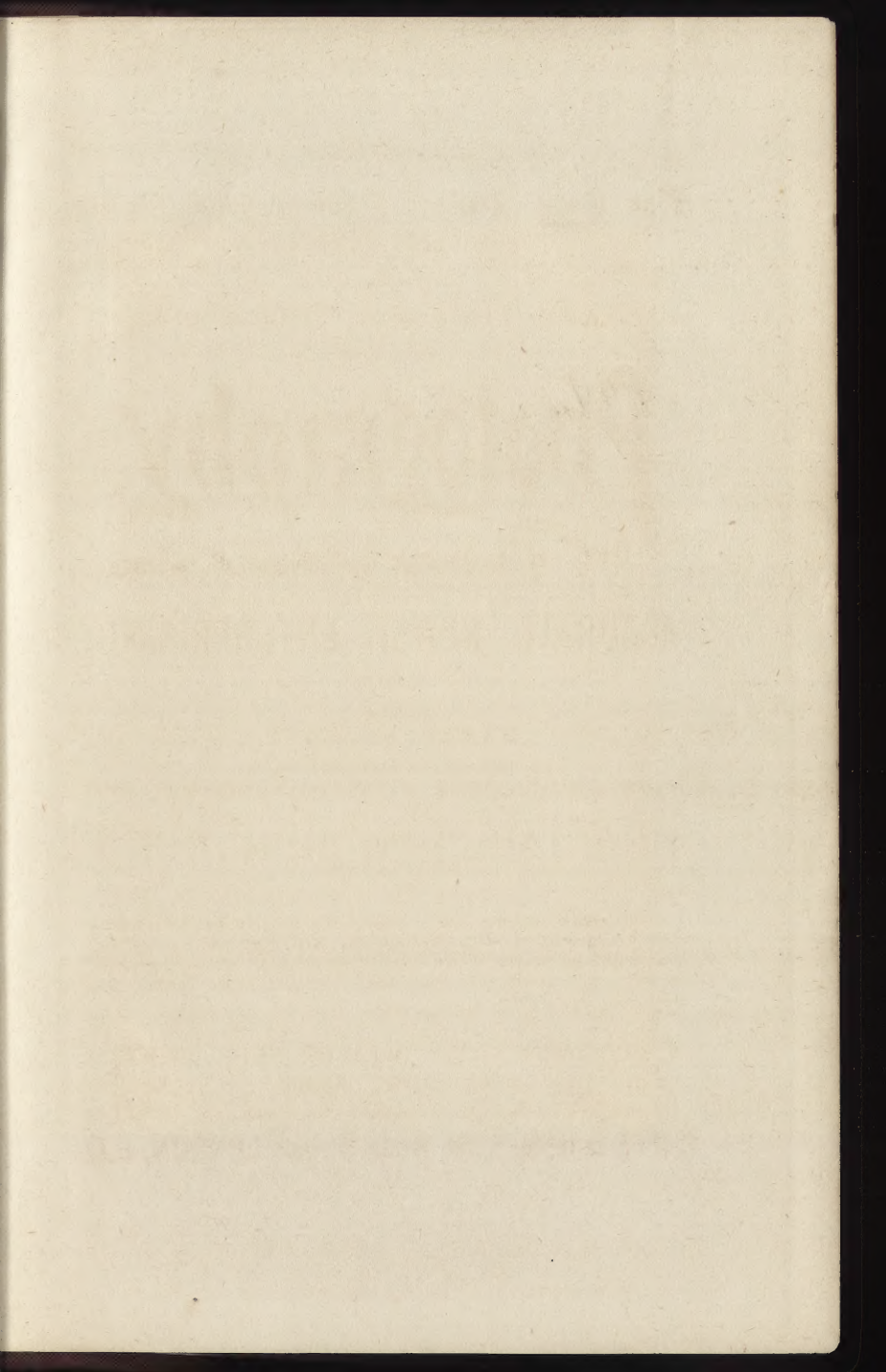
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